PROCEEDINGS

OF

THE CHEMICAL SOCIETY.

Vol. XXIII. Nos. 319—334.

JANUARY—DECEMBER, 1907.

LONDON:

GURNEY & JACKSON, 10, PATERNOSTER ROW.

1908.

RICHARD CLAY AND SONS, LIMITED,
BREAD STREET HILL, E.C., AND
BUNGAY, SUFFOLK.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR 1907.

£20 to E. C. C. Baly: the ultra-violet absorption spectra of organic compounds (continued).

£10 to A. T. Cameron: the physical constants of the potassium salts of succinic acid and its homologues.

£25 to J. A. Carpenter: experiments with highly purified gases.

£5 to A. E. Dunstan: the application of viscosity to the question of the existence of racemates in the liquid state.

£5 to C. E. Fawsitt: the viscosity of fluid substances (including metals) and the physico-chemical properties of solids in different states (phases) (continued).

£15 to K. Fisher: separation of tetrahydro-*p*-toluic acid into its optically active modifications, and attempt to synthesise sylvestrene.

£15 to W. N. Haworth: preparation of terpenes and the synthesis of fenchone.

£5 to Miss Annie Homer: the products of the action of aluminium chloride on naphthalene.

£10 to T. M. Lowry: studies in dynamic isomerism (continued).

£15 to A. N. Meldrum: conversion of symmetrical hydroxy-*m*-toluic acid into its hexahydro-derivative, and attempt to synthesise a terpene.

£5 to T. S. Moore: the measurement of the true ionisation constants, and of the hydration constants of amines, pseudo-acids, and bases and lactones.

£5 to R. H. Pickard: the relationship between optical activity and chemical constitution.

£1. 14. 1 to F. G. Pope: the relation between colour and constitution in the azomethine series.

£20 to R. Robinson: synthesis of some of the more important oxidation products of brazilin.

£20 to J. L. Simonsen: synthesis of norpinic, pinic, and pinonic acids, and the oxidation products of pinene.

£5 to C. Smith: the constitution of hydroxyazo-compounds.

£10 to A. W. Stewart: the relation between the constitution and dielectric constants of various organic compounds.

£20 to J. J. Sudborough: "Steric Hindrance," polynitro-compounds, and derivatives of cinnamic acid (continued).

£12 to W. B. Tuck: the constitution of the oxyazo-compounds.

£15 to V. H. Veley: hydrolysis of hydrochlorides of bases by means of methyl-orange solution.

£15 to H. Watson: preparation of ketonic acids from methyl *cyclo*-hexanones.

£10 to E. A. Werner: the derivatives of multivalent iodine.

£10 to G. Young: heterocyclic compounds (continued).

Total amount granted during 1907 = £273. 14. 1.

LIST OF FELLOWS ELECTED DURING 1907.

Name.	Proposed.	Elected.
Allan, John Campbell	February 7th, 1907	May 2nd.
Allen, Alfred Frederick	December 20th, 1906.	February 21st.
Bagley, George	December 6th, 1906.	,, ,,
Bailey, Francis James	February 7th, 1907	May 2nd.
Baker, Frank	December 6th, 1906.	February 21st.
Ball, William Robert	February 21st, 1907.	May 2nd.
Banks, Arthur John	June 20th, 1907	December 5th.
Barnett, Edward de Barry	November 7th, 1907.	,, ,,
Bassett, Henry, jun.	December 20th, 1906.	February 21st.
Bell, John Forbes	October 24th, 1907	December 5th.
Benton, Frank Stanley	November 15th, 1906.	February 21st.
Berry, Leslie Hamilton	January 17th, 1907	,, ,,
Buckney, Frank	June 6th, 1907	December 5th.
Caldwell, Kenneth Somerville	March 21st, 1907	May 2nd.
Callan, Thomas	July 4th, 1907	December 5th.
Cameron, Alexander Thomas	February 21st, 1907	May 2nd.
Cart, John Trevor	November 15th, 1906.	February 21st.
Caton, Frederic William	November 7th, 1907.	December 5th.
Christie, John	December 20th, 1906.	February 21st.
Clough, George Wiliiam	November 15th, 1906.	,, ,,
Colebourn, William Arthur	May 16th, 1907	June 20th.
Cook, Taylor	December 6th, 1906.	February 21st.
Copping, Hugh Hague	April 18th, 1907	June 20th.
Cowap, Matthewman Dalton	,, ,, ,,	,, ,,
Crisp, George Hugh	November 7th, 1907.	December 5th.
Croghan, Edward Henry	November 21st, 1907.	,, ,,
Cunningham, John Arthur	March 7th, 1907	May 2nd.
Dall, Colin Ernest	December 6th, 1906.	February 21st.
Davidson, Francis	December 20th, 1906.	,, ,,
Day, Edward Joseph	October 24th, 1907	December 5th.
Dealy, Thomas Kirkman	April 18th, 1907	May 2nd.
Denham, William Smith	December 20th, 1906.	February 21st.
Dikshit, Mohan Nath Kedarnath	January 17th, 1907	,, ,,
Duckworth, Samuel	March 7th, 1907	May 2nd.
Dupré, Frederick Harold	October 24th, 1907	December 5th.
Dupré, Percy Vivian	,, ,, ,,	,, ,,
Dutton, Francis Bridger	,, ,, ,,	,, ,,
Eastaugh, Frederick Alldis	December 6th, 1906.	February 21st.
Elias, Owen Aubrey	May 2nd, 1907	June 20th.
Farmer, John Edwin	January 17th, 1907	February 21st.
Fawcitt, Claude Scott	November 7th, 1907.	December 5th.

Name.	Proposed.	Elected.
Fischer, Eugen	April 18th, 1907.	June 20th.
Foreman, Charles Thomas	November 21st, 1907.	December 5th.
Fowles, George	December 20th, 1906.	February 21st.
Fox, John Jacob	March 21st, 1907	May 2nd.
Foxell, Edward William Lanchester	December 6th, 1906.	February 21st.
Fryer, Percival John	January 17th, 1907.	,, ,,
Gibson, Charles Stanley	February 7th, 1907	May 2nd.
Gibson, William Howieson	December 6th, 1906.	February 21st.
Gledhill, Walter George	April 18th, 1907	June 20th.
Godden, William	December 20th, 1906.	February 21st.
Green, William Heber	January 17th, 1907.	,, ,,
Greenough, Thomas Rigby	October 24th, 1907	December 5th.
Gregory, Joshua Craven	February 7th, 1907.	May 2nd.
Grieb, Christopher Maurice Walter	December 6th, 1906.	February 21st.
Hall, Joseph Henry	March 21st, 1907.	May 2nd.
Harrington, Arthur George	March 7th, 1907	,, ,,
Harvey, Thomas Featherstone	March 21st, 1907	,, ,,
Hay, William	June 6th, 1907	December 5th.
Higham, Richard	January 17th, 1907	February 21st.
Hooton, William Marrs	December 6th, 1906.	,, ,,
Hope, Geoffrey Dodleston	February 21st, 1907.	May 2nd.
Houghton, Edward	March 21st, 1907.	,, ,,
Hoyten, William James	January 17th, 1907.	February 21st.
Hubbard, Hon. Raymond Egerton	February 21st, 1907.	May 2nd.
Hughes, Francis Townshend Cunynghame	January 17th, 1907.	February 21st.
Humphries, Herbert Brooke Perren	February 21st, 1907.	May 2nd.
Hussey, Arthur Vivian	December 6th, 1906.	February 21st.
Hutchinson, William Doge	October 24th, 1907.	December 5th.
Ingham, Harry	,, ,, ,,	,, ,,
Jackson, Ernest Wilfrid	December 6, 1906	February 21st.
Jackson Victor George	November 15th, 1906.	,, ,,
Jennings, John Atkinson	April 18th, 1907.	June 20th.
Jennings, Sidney James	January 17th, 1907.	February 21st.
Jensen, Charles William Lamb	May 16th, 1907	June 20th.
Jones, Benjamin Owen	July 4th, 1907.	December 5th.
Kaye, John	June 20th, 1907.	,, ,,
King, Albert Theodore	December 6th, 1906.	February 21st.
Lewis, Carl	March 21st, 1907	May 2nd.
Lloyd, Percival George	April 18th, 1907.	June 20th.
Lunan, George	January 17th, 1907.	February 21st.
McConnan, James	February 21st, 1907.	May 2nd.
Marsden, Herbert	October 24th, 1907.	December 5th.
Marshall, Hubert Frederick Sankey	,, ,, ,,	,, ,,
Martin, Gerald Hargrave	,, ,, ,,	,, ,,
Martin, Joseph	December 6th, 1906.	February 21st.
Matthews, Charles Pask	December 20th, 1906.	,, ,,
Mitchell, Herbert Victor	March 21st, 1907	May 2nd.

Name.	Proposed.	Elected.
Moore, John Edward Langford	October 24th, 1907	December 5th.
Mummery, Charles Samuel	,, ,, ,,	,, ,,
Murgatroyd, Louis	November 15th, 1906.	February 21st.
Nuttall, Walter Harold	May 2nd, 1907	June 20th.
Oberländer, Otto	December 6th, 1906	February 21st.
Pochin, Harold	April 18th, 1907	June 20th.
Remfry, Frederic George Percy	December 6th, 1906	February 21st
Rhodes, Percy Joseph	February 21st, 1907	May 2nd.
Rixon, Frederic William	March 7th, 1907	,, ,,
Robertson, Robert	November 15th, 1906	February 21st.
Robinson, John	February 7th, 1907	May 2nd.
Sahni, Ruchi Ram	May 16th, 1907	June 20th.
Salway, Arthur Henry	November 15th, 1906	February 21st.
Saunders, George Joseph	June 6th, 1907	December 5th.
Schlienger, Charles	December 20th, 1906.	February 21st.
Schober, William Bash	June 20th, 1907	December 5th.
Sewell, William George	December 20th, 1906.	February 21st.
Shepheard, Frederick George	,, ,, ,,	,, ,,
Smith, Robert Harry	July 4th, 1907	December 5th.
Smith, Robert Low	November 15th, 1906.	February 21st.
Smith, Sidney William	February 21st, 1907	May 2nd.
Stobie, Harold Ramsay	October 24th, 1907	December 5th.
Sturrock, George Colleymore	March 21st, 1907	May 2nd.
Sutcliffe, Sam Mortimer	,, ,, ,,	,, ,,
Tarr, Nicholas	February 21st, 1907	,, ,,
Tebb, William Scott	,, ,, ,,	,, ,,
Templeton, William Sandilands	November 15th, 1906.	February 21st.
Thomas, Frederick	October 24th, 1907	December 5th.
Thomas, Richard Noel Garrod	December 6th, 1906	February 21st.
Timpany, Harold Munkman	October 24th, 1907	December 5th.
Tinkler, Charles Kenneth	April 18th, 1907	June 20th.
Toch, Maximilian	November 15th, 1906	February 21st.
Tonner, William Griffiths	March 7th, 1907	May 2nd.
Twiney, William George	January 17th, 1907	February 21st.
Warner, Charles Horne	May 16th, 1907	June 20th.
Watkins, Charles Rowlatt	January 17th, 1907	February 21st.
Watson, George Arthur	October 24th, 1907	December 5th.
Wechsler, Marcus	June 20th, 1907	,, ,,
Wheeler, Edward	October 24th, 1907	,, ,,
Whymper, Robert	,, ,, ,,	,, ,,
Wight, Robert Burt	December 6th, 1906	February 21st.
Williams, Percy	October 24th, 1907	December 5th.
Williams, William Henry	January 17th, 1907	February 21st.
Willott, David	June 6th, 1907	December 5th.
Wilson, William John	October 24th, 1907	,, ,,
Wolff, Mark Arthur	December 6th, 1906	February 21st.
Wootton, Hubert Arthur	June 6th, 1907	December 5th.
Young, Walter Ormston	May 2nd, 1907	June 20th.
Zortman, Israel Hyman	,, ,, ,,	,, ,,

FELLOWS DECEASED, 1907.

Name.	Elected.	Died.
Aitken, Andrew Charles	February 7th, 1901	October 12th, 1907.
Andrews, Thomas	March 7th, 1870	June 19th, 1907.
Austen, Peter Townsend	February 17th, 1877	December 30th, 1907.
*Berthelot, Marcellin	March 1st, 1860	March 18th, 1907.
Bottle, Alexander	March 6th, 1873	October 4th, 1907.
Bowen, William	February 18th, 1903	January 29th, 1907.
Chapman, Edward	January 16th, 1868	July 25th, 1906.
Clark, John	December 7th, 1876	July 9th, 1907.
Dupré, August	January 19th, 1860	July 15th, 1907.
Gale, James	April 19th, 1866	February 12th, 1907.
Gamble, Sir David	March 17th, 1851	February 4th, 1907.
Hall, Samuel	June 1st, 1876	December 9th, 1907.
Harcourt, Leveson Francis Vernon	April 16th, 1863	September 14th, 1907.
Harrington, Bernard J.	June 17th, 1897	November 29th, 1907.
Ince, Joseph	February 7th, 1867	December 5th, 1907.
Keeling, Frank	December 20th, 1883	August 1st, 1906.
*Mendeléeff, Dmitri Ivanovitsch	February 1st, 1883	February 2nd, 1907.
*Menschutkin, Nicolai	January 20th, 1898	February 5th, 1907.
*Moissan, Henri	January 20th, 1898	February 20th, 1907.
O'Sullivan, Cornelius	April 20th, 1876	January 8th, 1907.
Page, Frederick James Montague	December 21st, 1871	August 16th, 1907.
Palmer, Arthur Charles	July 5th, 1906	December 5th, 1907.
Parfitt, Samuel	February 15th, 1906	November 18th, 1907.
Perkin, Sir William Henry	December 15th, 1856	July 14th, 1907.
Perkins, Hugh Donald	December 7th, 1905	March 19th, 1907.
Polkinghorne, Bennett Corcyra	December 7th, 1899	December 29th, 1907.
Pritchard, William	February 17th, 1870	November 20th, 1906.
Swann, Robert Reed	May 4th, 1905	November 19th, 1907.
Walker, John Francis	February 2nd, 1865	May 23rd, 1907.
Warington, Robert	March 19th, 1863	March 20th, 1907.
Wright, Herbert Edwards	December 6th, 1900	February 2nd, 1907.

* Honorary and Foreign Member.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1907.

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2. Organic derivatives of silicon. Part II. The synthesis of *dl*-benzylethylpropylsilicol, its sulphonation, and the resolution of the sulphonic derivative into optically active components. By Frederic Stanley Kipping ..	9	209
3. The association of phenols in the liquid condition. By John Theodore Hewitt and Thomas Field Winmill ..	10	441
4. A new mercuric oxychloride. By John Theodore Hewitt.	10	—
5. Preparation of chromyl dichloride. By Herbert Drake Law and Frederick Mollwo Perkin	11	191
6. Oxidation of hydrocarbons of the benzene series. By Herbert Drake Law and Frederick Mollwo Perkin ...	11	258
7. The constitution of silver nitrite; a correction. By Edward Divers	11	—
8. Aromatic selenonium bases. By Samuel Smiles and Thomas Percy Hilditch.....	12	—
9. The relation of colour and fluorescence to constitution. By Arthur George Green	12	—
10. Tetraketopiperazine. By Alfred Theophilus de Mouilpied and Alexander Rule	13	176
11. Transformations of highly substituted nitroaminobenzenes. II. *s*-Tribromo-1-nitroaminobenzene. By Alice Emily Smith and Kennedy Joseph Previté Orton	14	146
12. Resolution of tetrahydro-*p*-toluquinaldine into its optically active components. By Thomas Constantine Beck and William Jackson Pope...	15	458
13. Note on the theory of valency. By William Barlow and William Jackson Pope.....	15	—
14. The condensation products of triacetic lactone with acetoacetic ester and β-aminocrotonic ester. By Frederick Noel Ashcroft Fleischmann	16	250
15. Derivatives of multivalent iodine. Part II. Action of heat on *p*-iodoacetophenone dichloride, *p*-iodoacetanilidedichloride, and on the dichlorides derived from *o*-, *m*-, and *p*-iodotoluene. By William Caldwell and Emil Alphonse Werner	17	240
16. Disalicylamide. By James McConnan.....	18	196

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17. Benzoyl derivatives of *N*-methylsalicylamide. By James McConnan and Morris Edgar Marples	18	193
18. The velocity of reaction of bromine with some unsaturated acids in aqueous solution. By Ernest Barrett and Arthur Lapworth	18	—
19. Note on the molecular complexity of liquids. By Albert Ernest Dunstan and Ferdinand Bernard Thole.	19	—
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20. The rapid electro-analytical deposition and separation of metals. Part I. The metals of the silver and copper groups and zinc. By Henry Julius Salomon Sand	26	373
21. The alkaloids of ergot. By George Barger and Francis Howard Carr	27	337
22. Influence of substitution on the formation of diazoamines and aminoazo-compounds. Part VI. The partially methylated 4 : 6-diamino-*m*-xylenes. By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait	28	360
23. The constitution of umbellulone. Part II. The reduction of umbellulonic acid. By Frank Tutin.	28	271
24. The reduction of hydroxylaminodihydroumbellulone-oxime. By Frank Tutin	29	275
25. Studies on optically active carbimides. Part V. The aryl esters and the amides of *l*-menthylcarbamic acid. By Robert Howson Pickard and William Oswald Littlebury	30	300
26. Some constituents of natural indigo. Part I. By Arthur George Perkin and William Popplewell Bloxam	30	279
27. The occurrence of isatin in some samples of Java indigo. By Arthur George Perkin	30	—
28. The absorption spectra of benzoic acid, the benzoates, and benzamide. By Walter Noel Hartley and Edgar Percy Hedley	31	319
29. The absorption spectra of phthalic, *iso*phthalic, and terephthalic acids, phthalic anhydride, and phthalimide. By Walter Noel Hartley and Edgar Percy Hedley	31	314
30. $\alpha\alpha\gamma$-Trimethyl- and $\alpha\alpha\gamma\gamma$-tetramethyl-tricarballylic acids and $\alpha\delta$-dimethylbutane-$\alpha\beta\delta$-tricarboxylic acid. By Herbert Henstock and Charles Henry Graham Sprankling	32	354
31. A reaction of certain colouring matters of the oxazine series. By Jocelyn Field Thorpe	32	324
32. The alkylation of *d*-fructose. By Thomas Purdie and David McLaren Paul	33	289
33. A simple apparatus, with stirrer, for treating a liquid at its boiling point with two or more gases. By Norman Leslie Gebhard	34	—

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34. Note on the arsenates of lead and calcium. By Spencer Pickering	35	307
35. Camphor-β-sulphinic acid and camphorylsulphonium bases. By Samuel Smiles and Thomas Percy Hilditch	35	519
36. The condensation of salicylamide with aryl aldehydes. By Charles Alexander Keane and William Walter Scott Nicholls	36	264
37. The condensation of diethylmalonamide with aldehydes. By Harry Burrows and Charles Alexander Keane	36	269
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38. The constitution of hydroxyazo-compounds. By William Bradshaw Tuck	58	449
39. The influence of solvents on the rotation of optically active compounds. Part. IX. A new general method for studying intramolecular change. By Thomas Stewart Patterson and Andrew McMillan	60	504
40. Displacement of halogens by hydroxyl. I. The hydrolytic decomposition of hydrogen and sodium monochloroacetates by water and by alkali, and the influence of neutral salts on the reaction velocities. By George Senter	60	460
41. The interaction of ammonium salts and the constituents of the soil. By Alfred Daniel Hall and Conrad Theodore Gimingham	61	677
42. The reduction products of *o*-and *p*-dimethoxybenzoin. By James Colquhoun Irvine and Agnes Marion Moodie.	62	536
43. Constituents of natural indigo. Part II. By Arthur George Perkin	62	435
44. The velocity of hydrolysis of aliphatic amides. By James Codrington Crocker	63	593
45. The rusting of iron. By Wyndham Rowland Dunstan.	63	—
46. Contributions to the chemistry of the rare earths. Part II. By Mario Esposito	64	—
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48. The organic phosphorus compound formed by yeast-juice from soluble phosphates. Preliminary notice. By William John Young	65	—
49. Experiments on the synthesis of the terpenes. Part X. Synthesis of carvestrene and its derivatives. By William Henry Perkin, jun., and George Tattersall.	66	480
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50. The constitution of chaulmoogric and hydnocarpic acids. By Marmaduke Barrowcliff and Frederick Belding Power	70	557

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51. Hydrolysis of amygdalin by acids. By Robert John Caldwell and Stephen Lewis Courtauld	71	666
52. Mandelonitrile glucosides. Prulaurasin. By Robert John Caldwell and Stephen Lewis Courtauld	71	671
53. The hydrolysis of amygdalin by emulsin. By Samuel James Manson Auld	72	—
54. Electrolytic reduction. Part III. By Herbert Drake Law	73	748
55. New cerium salts. By Gilbert Thomas Morgan and Edward Cahen	74	475
56. Volume changes which accompany transformations in the system $Na_2S_2O_3 : 5H_2O$. By Harry Medforth Dawson and Colin Gyrth Jackson	75	552
57. Depression of the freezing point of aqueous solutions of hydrogen peroxide by potassium persulphate and other compounds. By Thomas Slater Price	75	531
58. The formation and reactions of imino-compounds. Part III. The formation of 1 : 3-naphthylenediamine and its derivatives from *o*-toluonitrile. By Ernest Francis Joseph Atkinson, Harry Ingham, and Jocelyn Field Thorpe	76	578
59. The action of ethylene dibromide and of propylene dibromide on the disodium derivative of diacetylacetone. By Alexander William Bain	77	544
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60. Synthesis of polypeptides. By Emil Fischer	82	—
61. Organic derivatives of silicon. Part III. *dl*-Benzylmethylethylpropylsilicane and experiments on the resolution of its sulphonic derivative. By Frederic Stanley Kipping	83	717
62. The reduction of carbon dioxide to formaldehyde in aqueous solution. Henry John Horstman Fenton	83	687
63. The mechanism of the rusting of iron. By Gerald Tattersall Moody	84	—
64. Influence of non-electrolytes and electrolytes on the solubility of sparingly soluble gases in water. The question of hydrates in solution. By James Charles Philip	85	711
65. A new class of organo-metallic compounds. Preliminary notice. Trimethylplatinimethyl hydroxide and its salts. By William Jackson Pope and Stanley John Peachey	86	—
66. Some compounds of guanidine with sugars. Part I. By Robert Selby Morrell and Albert Ernest Bellars.	87	1010
67. The action of aluminium chloride on naphthalene. Formation of $\beta\beta$-dinaphthyl, tetranaphthyl, and tetramethylerythrene. By Annie Homer	88	1103
68. Mercurous hyponitrite. By Prafulla Chandra Rây	89	1404

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69. The decomposition of mercurous and silver hyponitrites by heat. By Prafulla Chandra Rây and Atul Chandra Gañguli	89	1399
70. Studies in optical superposition. Part III. By Thomas Stewart Patterson and John Kaye	89	705
71. An extension of the benzoin synthesis. By Reginald William Lane Clarke and Arthur Lapworth	90	694
72. Interaction of starch and carbon disulphide. Xanthogenic esters of starch. By Charles Frederick Cross, Edward John Bevan, and John Frederick Briggs	90	612
73. The estimation of small quantities of nitrogen peroxide. By Robert Robertson and Sidney Scrivener Napper.	91	761
74. The evolution of nitrogen peroxide in the decomposition of guncotton. By Robert Robertson and Sidney Scrivener Napper	91	764
75. An isomeric change of dehydracetic acid. By John Norman Collie and Thomas Percy Hilditch	92	787
April 18*th*.		
76. The magnetic rotation of hexatriene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, and its relationship to benzene and other aromatic compounds, also its refractive power. By Sir William Henry Perkin	110	806
77. Aromatic azoimides. Part I. *p*-Hydroxyphenylazoimide. By Martin Onslow Forster and Hans Eduard Fierz	112	855
78. Measurement of the velocities of saponification of the *l*-menthyl and *l*-bornyl esters of the stereoisomeric mandelic acids. By Alexander McKenzie and Herbert Bryan Thompson	113	789
79. The constituents of the essential oil of American pennyroyal. Occurrence of a dextro-menthone. By Marmaduke Barrowcliff	114	875
80. Studies in the camphane series. Part XXIII. Oximes of camphorylsemicarbazide and camphorylazoimide. By Martin Onslow Forster and Hans Eduard Fierz.	114	867
81. The action of ethyl oxalate on thioacetanilide and its homologues. By Siegfried Ruhemann	115	797
82. The action of tribromopropane on the sodium derivative of ethyl acetoacetate. By Thomas Edward Gardner and William Henry Perkin, jun.	115	848
83. Indican. Preliminary note. By Arthur George Perkin and William Popplewell Bloxam	116	—
84. Cupric nitrite. By Prafulla Chandra Rây	117	1405
85. The action of hydrogen peroxide on potassium cyanide. By Orme Masson	117	1449
86. The reaction between calcium carbonate and chlorine water. By Arthur Richardson	118	—
87. The density of hydrogen chloride. By Robert Whytlaw Gray	119	—

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88. Di-iodocamphor. By James Ernest Marsh and Robert de Jersey Fleming Struthers	119	—
89. Acyl-ψ-derivatives of iminothiolcarbamic acid and their isomerides. By Augustus Edward Dixon and John Taylor	119	912
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90. The chemical action of the radium emanation. Part I. Action on distilled water. By Sir William Ramsay, K.C.B	132	931
91. Freezing-point curves of the menthyl mandelates. By Alexander Findlay and Evelyn Marion Hickmans.	132	905
92. The constitution of homo-eriodictyol. A crystalline substance from eriodictyon leaves. By Frederick Belding Power and Frank Tutin	133	887
93. The relation between valency and heats of combustion. Preliminary note. By Gervaise Le Bas	134	—
94. The velocity of hydrolysis of aliphatic amides by alkali. By James Codrington Crocker and Frank Harold Lowe	135	952
95. The addition of iodine to acetylenic acids. By Thomas Campbell James and John Joseph Sudborough	136	1037
96. The chemical changes induced in gases submitted to the action of ultra-violet light. By David Leonard Chapman, Samuel Chalwick, and John Edwin Ramsbottom	136	942
97. Studies of the perhalogen salts. Part. I. By Charles Kenneth Tinkler	137	996
98. The interaction of cyanodihydrocarvone, amyl nitrite, and sodium ethoxide. Part I. By Arthur Lapworth and Elkan Wechsler	137	977
99. Contributions on the chemistry of oxygen compounds. II. The compounds of cineol, diphenylsulphoxide, nitroso-derivatives, and the carbamides with acids and salts. By Robert Howson Pickard and Joseph Kenyon	138	896
May 16th.		
100. The relation between the crystalline form and the chemical constitution of simple inorganic substances. By William Barlow and William Jackson Pope	142	1150
101. Experimental investigation into the process of dyeing. By Julius Hübner	144	1057
102. Esterification constants of substituted acrylic acids. Part II. By John Joseph Sudborough and Ebenezer Rees Thomas	146	1033
103. The addition of bromine to the α- and β-chloro- and bromo-cinnamic acids and their methyl esters. By John Joseph Sudborough and Gwilym Williams	146	—

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104. The addition of bromine to unsaturated compounds. Part I. By John Joseph Sudborough and John Thomas	147	—
105. Separation of cadmium from zinc as sulphide in the presence of trichloroacetic acid. By John Jacob Fox	147	964
106. The mechanism of bromination of acylamino-compounds. Preliminary notice. By Julius Berend Cohen and William Ernest Cross	148	—
107. Mixed semi-ortho-oxalic compounds. By George Druce Lander	148	967
108. Some derivatives of γ-pyranol allied to certain derivatives of brazilein and hæmatein. (Preliminary communication.) By William Henry Perkin, jun., and Robert Robinson	149	—
109. Arsenic di-iodide. By John Theodore Hewitt and Thomas Field Winmill	150	962
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ADDITIONS TO THE LIBRARY DURING THE YEAR 1907.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 319.

Thursday, January 17th, 1907, at 8.30 p.m., Professor R. MELDOLA, F.R.S., President, in the Chair.

Messrs. P. S. Arup, W. C. Ball, and J. Hamer were formally admitted Fellows of the Society.

The PRESIDENT announced the decision of the Council that during the remainder of the present Session the Library shall be kept open for the use of Fellows every Thursday from 10 a.m. until 9 p.m., except on those evenings on which the Society meets when it will remain open until 10.30 p.m.

Certificates were read for the first time in favour of Messrs. :

Leslie Hamilton Berry, B.Sc., Penshurst, Croham Park Avenue, S. Croydon.
Mohan Nath Kedarnath Dikshit, 21, Burlington Road, Bayswater, W.
John Edwin Farmer, Blelsoe, New Road, Mitcham Junction.
Percival John Fryer, 27, Minster Road, Cricklewood, N.W.
William Heber Green, D.Sc., The University, Melbourne.
Richard Higham, 133, Mauldeth Road, Withington, Manchester.
William James Hoyten, M.R.C.S., F.R.C.P., 37, Ravelstoke Road, Wimbledon Park, S.W.

Francis Townshend Cunynghame Hughes, Major, Royal Mint, Calcutta, India.
Sidney James Jennings, B.Sc., 367, Queen's Road, New Cross, S.E.
George Lunan, 50, Garscube Terrace, Murrayfield, Edinburgh.
William George Twiney, B.Sc., St. Joseph's College, Colombo, Ceylon.
Charles Rowlatt Watkins, B.A., Aldenham School, Elstree, Herts.
William Henry Williams, Government Education Dept., Hong Kong.

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.
15th November, 1906.

GENTLEMEN,

I have the honour to forward to you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1907, to which I have affixed, as desired by them, the names of Professors Moissan and Ostwald.

The Committee, for reasons stated in the Report, have suggested new values for the atomic weights of bismuth, nitrogen, tantalum, and terbium, and they are further of opinion that alterations are needed in the atomic weights of silver and chlorine, but before recommending any change as regards these elements they consider it expedient to wait for fuller information of the results of determinations known to be in progress. The new values for silver and chlorine will, of course, have an influence upon a large number of atomic weights.

I am, Gentlemen,
Your obedient Servant,
T. E. THORPE.

The Hon Secretaries,
The Chemical Society,
Burlington House,
London, W.

Report of the International Committee on Atomic Weights, 1907.

Since the preparation of our last report, for 1906, a number of important memoirs upon atomic weights have appeared. The results obtained may be briefly summarised as follows:

Bismuth.—Work done at Erlangen under the direction of Gutbier (*Zeit. Elektrochem.*, 1905, **11**, 831) has been published in the form of

three doctoral dissertations (L. Birckenbach, 1905; H. Mehler, 1905; R. L. Janssen, 1906). Birckenbach, by synthesis of the oxide from the metal, found, in mean, Bi = 208·05. A series of reductions of the oxide gave Bi = 208·08. Mehler determined the ratio $BiBr_3 : AgBr$, and found Bi = 208·05. By synthesis of the sulphate from the metal, Janssen obtained the value Bi = 208·074. These determinations are concordant, and also agree with the earlier measurements by Schneider and Löwe and with a series by Marignac. The atomic weight of bismuth, therefore, is to be taken as 208·0 in round numbers, and the value 208·5, as hitherto given in our table, is too high.

Bromine.—Baxter's (*J. Amer. Chem. Soc.*, 1906, **28**, 1322) determinations of this constant are based upon the antecedent values Ag = 107·93 and Cl = 35·473. Eighteen syntheses of silver bromide gave, in mean, Br = 79·953. Thirteen experiments upon the conversion of AgBr into AgCl gave Br = 79·952.

Cadmium.—The memoir by Baxter, Hines, and Frevert (*ibid.*, 1906, **28**, 770) is a continuation of the research which was noted last year. Four ratios were measured with the following results, when Ag = 107·93:

$CdBr_2 : 2Ag.$	Cd = 112·470.
$CdBr_2 : 2AgBr.$	Cd = 112·464.
$CdCl_2 : 2Ag.$	Cd = 112·471.
$CdCl_2 : 2AgCl.$	Cd = 112·470.

Copper.—A series of analyses and syntheses of copper oxide by Murmann (*Monatsh.*, 1906, **27**, 351) gave the value Cu = 63·53. The data are not concordant, and the determinations are not entitled to much weight.

Iodine.—Gallo (*Gazzetta*, 1906, **36**, 116) has determined the atomic weight of iodine electrolytically, comparing the iodine liberated by a current with the silver deposited. His values range from 126·82 to 126·98, or, in mean, 126·89 when Ag = 107·93. This result is more nearly in accord with the determination by Stas than with the later measurements.

Nitrogen.—Gray's (*Trans.*, 1905, **87**, 1601) work upon the atomic weight of this element, noticed in our report for 1906, has since been published in full. His mean results are as follows: from the density of nitric oxide, N = 14·006; from the analysis of nitric oxide, N = 14·010; from the density of nitrogen, N = 14·008. The mean of all the determinations is N = 14·0085, or very nearly 14·01. This agrees closely with the earlier measurements by Guye, Rayleigh, and Leduc, and leaves no reasonable doubt but that the new value should replace the 14·04 as given in our annual table. In a later paper (*Trans.*, 1906, **89**, 1173) Gray has gathered corroborative evidence

from various sources, and has discussed Stas's ratios in order to discover their possible errors. Other discussions of similar purport are by Guye * and Scott (*Chem. News*, 1906, **93**, 20), but they are not final. Experimental evidence alone can reveal the cause of discrepancy between the new figure and the old.

Palladium.—Amberg (*Annalen*, 1905, **341**, 235) has redetermined the atomic weight of palladium by analysis of palladosoammine chloride, $PdN_2H_6Cl_2$. The value obtained is Pd = 106·688, or 106·7 nearly. Five other analyses of the same salt, by Krell (*Inaug. Dissertation*, Erlangen, 1906), gave a mean of Pd = 106·694. Recalculated with Richards's value for Cl, and rejecting one experiment as defective, Krell concludes that Pd = 106·78, but this again would be lowered by the adoption of the newer value for N. Any change in this constant may well be deferred until the antecedent atomic weights are more definitely known.

Silver.—In an attempt to determine the source of error in Stas's figures for nitrogen, Guye and Ter Gazarian † examined the fundamental potassium chlorate ratio. They found that potassium chlorate crystallises with a small quantity of chloride as an impurity, the amount being nearly constant and about 2·7 parts in ten thousand. Applying this correction to Stas's ratios, his value for silver is lowered from 107·93 to 107·89. A re-discussion of ten fundamental ratios gave figures for silver ranging from 107·871 to 107·908, or 107·89 in mean. If this conclusion is sustained, the Stas's ratios for silver nitrate will give a value for nitrogen in harmony with the figures obtained by Guye and Gray.

Tantalum.—Hinrichsen and Sahlbom (*Ber.*, 1906, **39**, 2600) have determined the atomic weight of tantalum by conversion of the metal into the pentoxide. Five such syntheses gave Ta = 180·59 to 181·77, or 181·0 in mean. This value should replace the old determination by Marignac as given in our previous tables.

The Rare Earths—On the metals of this group a notable amount of work has been published during 1906. From five determinations of water in terbium sulphate, Urbain (*Compt. rend.*, 1906, **142**, 957) deduces the value Tb = 159·22; and this should supplant the older, questionable data. In another paper (*ibid.*, 1906, **142**, 785) Urbain gives an atomic weight of 163·49 to dysprosium, but without details or weighings.

By a volumetric method, Feit and Przibylla (*Zeit. anorg. Chem.*, 1906,

* *Ber.*, 1906, **39**, 1470. For Guye and Bogdan's complete memoir upon nitrous oxide, see *J. Chim. phys.*, 1905, **3**, 537.

† *Compt. rend.*, 1906, **143**, 411. See also *J. Chim. phys.*, 1906, **4**, 174, for a paper by Guye on the need of a general recalculation of atomic weights.

50, 249) have determined the amount of sulphuric acid required to neutralise several of the oxides in this group, and have in that way obtained new estimates of the corresponding atomic weights. The final results, reduced to a vacuum standard, are as follows :

Lanthanum	139·17	Europium	152·66
Praseodymium	140·62	Gadolinium	157·38
Neodymium	144·52	Ytterbium	173·52
Samarium	150·47	Yttrium	89·40

In Abegg's *Handbuch der anorganische Chemie*, Brauner has given full summaries of all atomic weight determinations. With these summaries, in connexion with the rare earth metals (in Bd. 3, Abth. 1, pp. 263, 276, 284, 304, 318, 335), he has cited some hitherto unpublished determinations of his own. His results are :

Praseodymium	140·97	Gadolinium	155·78
Neodymium	143·89	Erbium	167·14
Samarium	150·71	Ytterbium	173·08

Among these figures that for Gd is admittedly too low, and that for Sa is vitiated by the presence of europium in the material studied.

From the evidence presented in this report, and in preceding years, we now feel justified in recommending the following changes in the table :

Nitrogen,	from	14·04	to 14·01.
Bismuth,	„	208·5	„ 208·0.
Tantalum,	„	183·0	„ 181·0.
Terbium,	„	160·0	„ 159·2.

Other changes which seem to be needed because of alterations in the atomic weights of silver and chlorine cannot yet be made with safety. The atomic weight of silver, as deduced from Stas's data, is probably too high, but by an unknown amount, and that will affect the entire table. If we assume, with Guye, that Ag = 107·89, with the proportional changes in Cl and Br, the atomic weight of barium, as determined by Richards, will be reduced by 0·05. Such a change, which is probably extreme, does not affect the utility of the accepted atomic weights at all seriously, and no important interest will suffer if we delay the suggested alterations until our knowledge of the corrections to be applied is more exact. Guye's conclusions, although strongly supported, are not final, and they should be neither accepted nor rejected except upon the basis of much more complete evidence

than we now possess. The atomic weight of chlorine, as given in our last report, is certainly too low, but it depends in part upon the undetermined change to be applied to silver. For that reason, as well as for the reason that a change in chlorine affects many other values, we prefer to leave the figures as they are and to wait for fuller information. That information will doubtless be supplied by researches now known to be in progress, and the corrections which they will furnish ought not to be delayed very long.

One addition to the table seems to be legitimate. Europium, with an approximate atomic weight of 152, appears to be a definite element, as shown by the investigations of Demarçay, Urbain and Lacombe, Eberhard, and Feit and Przibylla. Its existence is recognised in Abegg's Handbuch, and its claims to a place in the table are certainly as great as those of erbium, thulium, or terbium. As for dysprosium, its admission to the table may well be delayed until a better determination of its atomic weight shall have been made.

In conclusion, we urge upon all chemists who are engaged in the determination of atomic weights to send copies of their publications to all the members of this committee in order that their work may be promptly recognised and not overlooked. Data published in standard journals are of course easily found, but publications of local societies and doctoral dissertations might readily escape our notice.

Professor Seubert, an original member of this committee, has resigned. Professor Ostwald has been designated as his successor.*

The table offered for 1907 is appended hereto.

F. W. Clarke,
Henri Moissan,
Wilhelm Ostwald,
T. E. Thorpe.

* See *Ber.*, 1906, **39**, 2176, for the formal announcement of this change.

1907.

International Atomic Weights.

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·4
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·96
Cadmium	Cd	112·4
Cæsium	Cs	132·9
Calcium	Ca	40·1
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·45
Chromium	Cr	52·1
Cobalt	Co	59·0
Columbium	Cb	94
Copper	Cu	63·6
Erbium	Er	166
Europium	Eu	152
Fluorine	F	19·0
Gadolinium	Gd	156
Gallium	Ga	70
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	1·15
Iodine	I	126·97
Iridium	Ir	193·0
Iron	Fe	55·9
Krypton	Kr	81·8
Lanthanum	La	138·9
Lead	Pb	206·9
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Neon	Ne	20
Nickel	Ni	58·7
Nitrogen	N	14·01
Osmium	Os	191
Oxygen	O	16·00
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	194·8
Potassium	K	39·15
Praseodymium	Pr	140·5
Radium	Rd	225
Rhodium	Rh	103·0
Rubidium	Rb	85·5
Ruthenium	Ru	101·7
Samarium	Sa	150·3
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·05
Strontium	Sr	87·6
Sulphur	S	32·06
Tantalum	Ta	181
Tellurium	Te	127·6
Terbium	Tb	159·2
Thallium	Tl	204·1
Thorium	Th	232·5
Thulium	Tm	171
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium	Yb	173·0
Yttrium	Yt	89·0
Zinc	Zn	65·4
Zirconium	Zr	90·6

Of the following papers, those marked * were read :

***1. "The relation between absorption spectra and optical rotatory power. Part I. The effect of unsaturation and stereoisomerism." By Alfred Walter Stewart.**

The author has examined the absorption spectra of certain saturated and unsaturated acids, and compared the results with the rotatory power of their amyl esters. The results show that a close relation exists between the general absorption power of compounds and their molecular rotation. The substance having the greater general absorption has also the greater molecular rotation. The case of the amyl esters of hydrocinnamic, cinnamic, and phenylpropiolic acids, which seems anomalous at first sight, agrees with this. An examination of the spectra of some stereoisomeric acids of the ethylene series showed that the rule holds in their case also. Experiments are in progress in other branches of the subject, for example, active and inactive isomerides, birotation, the influence of the solvent on the rotatory power, &c.

Discussion.

Dr. McKenzie pointed out that the values for the molecular rotations of the amyl esters of hydrocinnamic, cinnamic, and phenylpropiolic acid respectively, determined by Walden and quoted by the author, were obviously incorrect, since the amyl alcohol used by Walden in 1896 was a mixture.

Since it was now possible to separate the optically active constituent of fusel oil in a pure state by means of 3-nitrophthalic acid (*Ber.*, 1901, **34**, 485), he asked whether the author had prepared the pure esters in question and determined their rotations.

Mr. Stewart explained that owing to the complexity of the amyl spectrum it had been found best to examine the spectra of the acids and not those of the amyl esters. The cause of the change in rotation evidently is to be sought in the acidic part of the ester molecule. The results obtained by Sir W. H. Perkin in the case of the magnetic rotation of saturated and unsaturated acids agree with those observed in the case of optically active esters of the saturated and unsaturated series.

***2. "Organic derivatives of silicon. Part II. The synthesis of *dl*-benzylethylpropylsilicol, its sulphonation, and the resolution of the sulphonic derivative into optically active components." By Frederic Stanley Kipping.**

dl-*Benzylethylpropylsilicol*, $EtPrBzSi{\cdot}OH$, has been synthesised by the following series of reactions (compare *Proc.*, 1904, **20**, 15):

$SiCl_4 + MgEtBr = SiEtCl_3 + MgClBr.$

$SiEtCl_3 + MgPhBr = SiEtPhCl_2 + MgClBr.$

$SiEtPhCl_2 + MgPrBr = SiEtPhPrCl + MgClBr.$

$SiEtPhPrCl + MgBzCl = SiEtPhPrBz + MgCl_2.$

$SiEtPhPrBz + H_2O(+H_2SO_4) = SiEtPrBz{\cdot}OH + C_6H_6(+H_2SO_4).$

The silicol thus initially produced yields, with sulphuric acid, a mixture of sulphonic acids of which one has been isolated in the form of its ammonium salt.

This acid is probably a derivative of the corresponding oxide, having the constitution $SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtPr{\cdot}O{\cdot}PrEtSi{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$; it is the externally compensated compound, and although many of its salts with optically active bases crystallise unchanged, the *d*-methylhydrindamine salt can be resolved by crystallising fractionally from aqueous methyl alcohol.

The *dBdA*-salt is the more sparingly soluble and melts at about 205°; the impure *dBlA*-salt from the most soluble fractions melts at about 135°.

The *lBlA*-salt has been prepared by resolving the acid with *l*-methylhydrindamine.

The two optically active acids have very low specific rotations ($[\alpha]_D \pm 4°$ roughly), but there is ample evidence of their enantiomorphous relationship.

Discussion.

Dr. Lewkowitsch, referring to the statement that different melting points were obtained with one and the same substance, asked whether this phenomenon was accompanied by the appearance of different colours, such as Jaeger had observed in the case of the liquid anisotropic phases of the esters of cholesterol and phytosterol at their different melting points.

Prof. Kipping stated that the appearance of such colours had not been observed by him.

***3. "The association of phenols in the liquid condition." By John Theodore Hewitt and Thomas Field Winmill.**

The authors have determined the surface energy of several liquids, and find that the association of phenols is diminished or entirely inhibited by the presence of ortho-substituents. Comparison with meta- and para-isomerides has clearly shown that the effect is due more to the position than to the nature of the substituent group.

The effect of steric hindrance is also seen with the aromatic alcohols. Monophenylcarbinol (benzyl alcohol) is markedly associated at the ordinary temperature; the molecular weights of fused di- and triphenylcarbinol are, however, normal.

DISCUSSION.

Dr. HEWITT, replying to the remarks of the President, said he supposed that probably they (the authors) had not encountered the best conditions for converting *o*-aminophenol into *o*-bromophenol. Respecting Mr. Baly's contention that any hindrance to association was structural rather than sterical, it was at least remarkable that the groups of larger molecular volume had a more marked effect than those, such as methyl and chlorine, whose molecular volume was smaller.

***4. "A new mercuric oxychloride." By John Theodore Hewitt.**

On allowing solutions of sodium hydroxide and mercuric chloride in sodium chloride to diffuse into one another, a layer of sodium chloride solution of intermediate density being interposed, very dark red crystals having the formula $Hg_6O_5Cl_2$ are deposited. These were at first considered to be red mercuric oxide or mercuric hydroxide, since on solution in hot dilute nitric acid and addition of silver nitrate solution no precipitate was obtained.

It has now been found that if a silver chloride precipitate is suspended in dilute nitric acid and mercuric oxide added, not only is the latter dissolved but also the silver chloride.

In the estimation of chlorine in the oxychloride the latter was dissolved in warm dilute sulphuric acid, the mercury precipitated with sodium hyposulphite, and after oxidation of the excess of this reagent with dilute nitric acid, the chlorine was estimated in the usual way as silver chloride.

DISCUSSION.

Dr. HEWITT was afraid he had not made the fact quite clear, that when silver chloride is dissolved in dilute nitric acid by addition

of mercuric oxide the result is not to be attributed to the formation of a complex silver ion, but to the employment of the chlorine in forming complex ions with the mercury. The solubility of silver salts in albumenoid solutions mentioned by Dr. Divers was hardly of a similar nature, in the latter case solution depended rather on colloidal suspension.

***5. "Preparation of chromyl dichloride." By Herbert Drake Law and Frederick Mollwo Perkin.**

The authors find that the best method for preparing chromyl dichloride is to dissolve chromic acid in rather more than the equivalent quantity of concentrated aqueous hydrochloric acid and to add to this solution concentrated sulphuric acid in small quantities at a time, the mixture being cooled between each addition. After standing for about twenty minutes in a tap funnel the heavy under layer of chromyl dichloride is drawn off. It can be purified by aspirating dry air through it and subsequent distillation. The yield is almost theoretical.

***6. "Oxidation of hydrocarbons of the benzene series." By Herbert Drake Law and Frederick Mollwo Perkin.**

The authors have examined the products of oxidation of aromatic hydrocarbons by lead peroxide and manganese peroxide in acid solution, by chromyl dichloride and by persulphates in acid solution in presence of silver salts.

The hydrocarbons investigated were toluene, the three xylenes, mesitylene, ψ-cumene, and cymene. In all cases varying yields of the monoaldehydes were obtained.

Toluene gave with lead peroxide 24 per cent. of benzaldehyde, with manganese peroxide 5 per cent., with chromyl dichloride 44 per cent., and with persulphates 78 per cent. In the remaining cases, as a rule, the yield with chromyl dichloride was better than with the other oxidising agents, that obtained with persulphates being second. In general, lead peroxide gave a larger quantity of aldehyde than did manganese peroxide.

7. "The constitution of silver nitrite; a correction." By Edward Divers.

In the opening paragraph of a paper which has just appeared (*Trans.*, 1906, **89**, 1900), Rây and Neogi state that the present writer is inclined to accept as fairly conclusive the evidence which they have adduced in favour of the oxylic constitution of silver nitrite.

In his note in the Proceedings (1905, **21**, 281), to which they make reference, no opinion at all is expressed as to the constitution of silver nitrite. The authors must have made the statement under some misapprehension of the writer's words, which he cannot account for.

8. "Aromatic selenonium bases." By Samuel Smiles and Thomas Percy Hilditch.

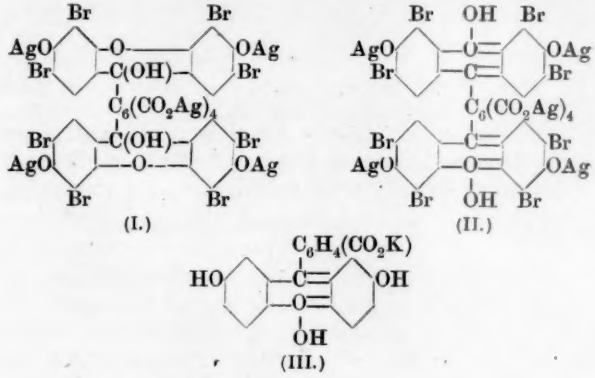
When anisole or phenetole are heated on the water-bath with selenium dioxide and aluminium chloride, the chlorides of the corresponding selenonium bases are formed. To isolate these substances, the reaction mixture is decomposed with water and freed from excess of phenolic ether by distillation in steam; finally the mixture is extracted with chloroform which, on evaporation, leaves the chloride of the base as a red oil. *Trianisyl-* and *triphenetyl-selenonium chlorides* are viscous oils, the aqueous solutions of which yield strongly basic *hydroxides* on treatment with silver oxide. The *iodides* are sparingly soluble oils. The *platinichlorides* were obtained as brown precipitates, insoluble in water and very soluble in acetone. The *platinichloride* of *triphenetylselenonium* melts at 82—83°. The dichromates of these bases are insoluble in water and are precipitated in yellowish-brown flakes when an acid solution of potassium chromate is added to solutions of the chlorides. They are very unstable and turn dark on exposure to the air. *Trianisylselenonium dichromate* melts at 65—70°.

9. "The relation of colour and fluorescence to constitution." By Arthur George Green.

In a paper bearing the above title (*Trans.*, 1906, **87**, 1787), O. Silberrad has recently described a number of complex phthaleins formed by the condensation of mellitic and pyromellitic acids with resorcinol. From the fact that the silver salts of these phthaleins correspond to the substitution of hydrogen by silver, not only in all the carboxyl groups of the mellitic residue, but also in the two phenolic hydroxyl groups of each xanthene ring, it is concluded that "neither the colour nor the fluorescence of these compounds is dependent on the presence of quinone linkings, for in many cases a quinonoid structure is impossible." This conclusion Silberrad is inclined to extend to the phthaleins in general.

A study of the phthaleins of phenol and quinol, which the author has had in progress for some time past, has brought to light several facts pointing to an opposite conclusion and strongly confirming the view that the coloured salts of these phthaleins have a quinonoid structure. It therefore appears advisable to point out that Silberrad's

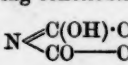
deductions are in no sense necessary, but that on the contrary his compounds may be represented with equal or greater probability upon a quinonoid type. For instance, in place of the carbinol formula (I) for the silver salt of the octabromohexahydroxy-*p*-dixanthylbenzenetetracarboxylic acid, the orthoquinone formula (II) may be substituted. The latter is analogous to (III), the formula proposed by the author for the potassium salt of quinolphthalein (*Ber.*, 1906, **39**, 2365):



10. "Tetraketopiperazine." By Alfred Theophilus de Mouilpied and Alexander Rule.

The authors have studied the action of sodium alkyloxides on esters of the type of ethyl oxamate, $NH_2 \cdot CO \cdot CO_2Et$, whereby the elimination of 1 molecule of alcohol would be expected to give rise to ring compounds containing an imino-group. Ethyl oxamate should by such a reaction furnish oxalimide, $\begin{matrix} CO \\ | \\ CO \end{matrix}\!\!>\!NH$, which is referred to by Ost and Mente (*Ber.*, 1886, **19**, 3228), but its existence appears to be very doubtful. The authors were not able to obtain it, but prepared from ethyl oxamate, *tetraketopiperazine*, which has twice the molecular weight of oxalimide and which seems to be the substance described under the latter name.

Tetraketopiperazine was also obtained by the condensation of ethyl oxalate with oxamide; a *hydrazone*, *silver* and *sodium* salts have been prepared, and the following constitutional formula is suggested:



Methyl succinamate yields succinimide by a similar reaction, and ethyl malonamate gives a *substance* of formula $C_6H_8O_5N_2$, resulting

from the condensation of 2 molecules of malonamic acid through loss of 1 molecule of water.

A general method for the preferential saponification of a carboxyalkyl group occurring in the same compound with an acid amide group was described.

Saponified with alkali in the usual way, ethyl oxamate yields the semi-ethyl ester and oxalic acid, and ammonia is simultaneously evolved. By using the theoretical amount of pure sodium alkyloxide in dry benzene solution a large yield of sodium oxamate is obtained.

11. "Transformations of highly substituted nitroaminobenzenes. II. *s*-Tribromo-1-nitroaminobenzene." By Alice Emily Smith and Kennedy Joseph Previté Orton.

Treatment of 2 : 4 : 6-tribromo-1-nitroaminobenzene,

$$C_6H_2Br_3\cdot NH\cdot NO_2,$$

with sulphuric acid or a mixture of sulphuric and acetic acids leads to the replacement of a bromine atom by the nitro-group, and to the formation of 2 : 6-dibromo-4-nitroaniline (*Trans.*, 1902, **81**, 806). Within very narrow limits of temperature and concentration of the sulphuric acid, the nitroamine is partly converted into bromophenyliminobenzoquinones, analogous to the hexachlorophenyliminobenzoquinone obtained from *s*-trichloronitroaminobenzene (*Trans.*, 1905, **87**, 389). In the case of the bromo-compounds, however, a mixture of two phenyliminobenzoquinones is always formed, namely, a penta- and a hexa-bromo-derivative, $C_6H_2Br_3\cdot N{:}C_6H_2Br_2{:}O$ and

$$C_6H_2Br_3\cdot N{:}C_6HBr_3{:}O;$$

bromine is accordingly set free in the reaction.

s-*Tribromophenyliminodibromobenzoquinone* crystallises in dark red prisms or needles with a metallic lustre, and melts at 171°. On reduction it yields s-*tribromophenyldibromo*-4-*hydroxyphenylamine*, which crystallises in white, silky needles melting at 155—156°, and is freely soluble in alcohol and other solvents. The latter can thus be separated from the s-*tribromophenyltribromo*-4-*hydroxyphenylamine*, which crystallises in colourless needles or prisms melting at 206°. On oxidation it is converted into s-*tribromophenyliminotribromobenzoquinone*, which crystallises in pale red needles or prisms melting at 134—135°, and is more soluble than the pentabromo-derivative in all the usual solvents.

12. "Resolution of tetrahydro-*p*-toluquinaldine into its optically active components." By Thomas Constantine Beck and William Jackson Pope.

The *d*-*aβ*-bromocamphorsulphonic acid of Armstrong and Lowry was shown to be applicable for the resolution of externally compensated bases, in accordance with the method of Pope and Peachey, by using it for the separation of the optically active tetrahydro-*p*-toluquinaldines from the corresponding externally compensated mixture. By treating two equivalents of *dl*-tetrahydro-*p*-toluquinaldine hydrochloride with one equivalent of the ammonium salt of the Armstrong and Lowry acid, under appropriate conditions, a nearly quantitative separation of *d*-tetrahydro-*p*-toluquinaldine-*d*-*aβ*-bromocamphorsulphonate is obtained; the salt gives the value $[M]_D + 445°$ in aqueous solution. On treating the base retained by the mother liquors with Kipping and Pope's *d*-bromocamphorsulphonic acid, nearly the whole of the *l*-base can be separated in a pure state as described by Pope and Rich.

The molecular rotatory powers of a number of salts of the optically active bases have been examined and found to be in agreement with previous conclusions concerning these values for salts of strong optically active bases with strong acids.

13. "Note on the theory of valency." By William Barlow and William Jackson Pope.

The homogeneous, close-packed assemblages of spheres corresponding to a series of homologous compounds, such as, for instance, the normal paraffins, are characterised by similarity of marshalling. Further, the assemblage representing ethane is derived from that of methane (*Trans.*, 1906, **89**, 1743) by an application of the second geometrical property (*loc. cit.*, 1729); the substitution of one carbon sphere of volume 4 for a hydrogen sphere of volume 1 in each unit, CH_4, of the partitioning of the methane assemblage necessitates the simultaneous addition of three hydrogen spheres in accordance with the second geometrical property, so that each unit of the ethane partitioning assumes the composition C_2H_6.

The empirical compositions, CH_3 and CH_4, of the ethane and methane assemblages differ, however, by one hydrogen sphere and a case is thus provided in which, so far as the packing of the spheres is concerned, two hydrogen spheres of volume 1 in the methane assemblage perform the functions of one hydrogen sphere of volume 1 in the ethane assemblage. This is therefore a case of the kind which Mr. D. L. Chapman (*Proc.*, 1906, **22**, 320) considers to offer difficulty

in connexion with our theory of valency and to necessitate some modification of the fundamental assumptions. From the fact that the methane and ethane assemblages are related through the second geometrical property, it is, however, clear that the application of Mr. Chapman's argument to an actual instance merely brings out the very close correspondence between the geometrical properties in question and our knowledge of chemical constitution.

Just as the bearings of the doctrine of valency on constitution and substitution do not appear when empirical compositions are considered, so the second geometrical property only serves to elucidate the doctrine of valency when it is applied in connexion with the molecular composition or the composition of the unit of the geometrical partitioning of the assemblage. A number of examples of the mode in which the property is applied have been already given (*loc. cit.*, 1729—1736).

We may perhaps be allowed to take this opportunity of emphasising the statement (*loc. cit.*, 1691 and 1698) that the geometrical properties and the assemblages, which latter are for diagrammatic purposes represented as if composed of undeformed spheres, are in every case supposed to be subject to the condition that so much general pressure is operative on the system as practically to eliminate the interstitial space. It is, of course, not conceivable that the space occupied by the spheres of influence of a group of atoms in contact should include space unavailable for occupation by the atoms.

14. "The condensation products of triacetic lactone with aceto-acetic ester and β-aminocrotonic ester." By Frederick Noel Ashcroft Fleischmann.

Triacetic lactone condenses in presence of strong sulphuric acid and hydrochloric acid, &c., with aceto-acetic ester, to form a *pyrone-lactone*, $C_{10}H_8O_4$, melting at 214°. The substance is extremely stable towards acids, but unstable in presence of alkalis, with which it forms deep yellow solutions. It yields a stable *bromo*-compound (m. p. 190°) crystallising from benzene with benzene of crystallisation, and a *nitro*-derivative (m. p. 200° approx.) which on treatment with strong aqueous ammonia yields aminodehydracetic acid. An unstable abnormal *barium* salt was also prepared, from which an insoluble, unstable *silver* and a *mercuric* salt were obtained.

A similar condensation takes place between triacetic lactone and β-aminocrotonic ester in presence of sulphuric, hydrochloric, or glacial acetic acids. The same pyrone-lactone is produced and, in the last instance, a second compound corresponding to the formula $C_{16}H_{19}O_6N$, the constitution of which is proved by its yielding the ethyl ester of ψ-lutidostyrilcarboxylic acid on treatment with alcoholic potash.

15. **"Derivatives of multivalent iodine. Part II. Action of heat on *p*-iodoacetophenone dichloride, *p*-iodoacetanilide dichloride, and on the dichlorides derived from *o*-, *m*-, and *p*-iodotoluene." By William Caldwell and Emil Alphonse Werner.**

One of us (Werner, *Trans.*, 1906, **89**, 1632) has shown that *p*-iodoacetophenone dichloride and *p*-iodoacetanilide dichloride when heated decompose with probable formation of substitution derivatives, thus differing from the general decomposition which has been hitherto recognised in connexion with the chlorides derived from tervalent iodine.

When *p*-iodoacetophenone dichloride, $CH_3 \cdot CO \cdot C_6H_4 \cdot ICl_2$, is heated (Werner, *Trans.*, 1906, **89**, 1632) it decomposes suddenly at 93—94°, only traces of chlorine (0·43 per cent.) being evolved in the free state, and *chloro*-p-*iodoacetophenone* is produced to the extent of 98 per cent. of the theoretical, thus:

$$CH_3 \cdot CO \cdot C_6H_4 \cdot ICl_2 = CH_2Cl \cdot CO \cdot C_6H_4I + HCl.$$

It forms long, slender prisms (m. p. 126—127°), and on oxidation it furnishes *p*-iodobenzoic acid. With chlorine it yields

$$CH_2Cl \cdot CO \cdot C_6H_4 \cdot ICl_2,$$

which decomposes at 128—130° with production of *dichloro*-p-*iodoacetophenone*, $CHCl_2 \cdot CO \cdot C_6H_4I$ (m. p. 62—63°). This also gives *p*-iodobenzoic acid on oxidation and unites with chlorine to form

$$CHCl_2 \cdot CO \cdot C_6H_4 \cdot ICl_2,$$

which is decomposed by heat with evolution of most of the chlorine in the free state.

p-Iodoacetanilide dichloride, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot ICl_2$, decomposes at 105° and yields *chloro*-p-*iodoacetanilide*, $CH_3CO \cdot NH \cdot C_6H_3ClI$ (m. p. 144°), from which a *chloroiodoaniline*, $C_6H_3ClI \cdot NH_2$ ($NH_2 : I : Cl = 1 : 4 : 2$ or 3) (m. p. 73°), is obtained. The *picrate* melts at 132°.

Chloro-*p*-iodoacetanilide unites with chlorine, forming

$$CH_3CO \cdot NH \cdot C_6H_3Cl \cdot ICl_2,$$

which decomposes at 131° and yields a substitution product which has not yet been investigated.

The action of heat on the chlorides of *o*-, *m*-, and *p*-iodotoluenes, prepared by Willgerodt, has been examined.

o-Tolyliodochloride decomposes at 85—86° and yields *o*-iodobenzyl chloride, $C_6H_4I \cdot CH_2Cl$, which gives *o*-iodobenzoic acid on oxidation.

m-Tolyliodochloride decomposes at 88°, giving an iodochloride which yields on oxidation an acid melting at 210° and containing both chlorine and iodine.

p-Tolyliodochloride decomposes at 110°, giving *p*-iodobenzyl chloride. In each case a small proportion of the original iodotoluene is regenerated.

16. "Disalicylamide." By James McConnan.

O-Salicylsalicylamide does not possess the properties previously attributed to it (*Patentschrift* No. 111, 656); the compound thus named by Cohn was probably disalicylamide.

Under suitable conditions, *O*-salicylsalicylamide rearranges, forming disalicylamide and *vice versâ*; this is another case of the metoxazone tautomerism peculiar to acyl derivatives of salicylamide, and already studied in the cases of the benzoyl and the acetyl derivatives (McConnan and Titherley, *Trans.*, 1906, **89**, 1318).

17. "Benzoyl derivatives of *N*-methylsalicylamide." By James McConnan and Morris Edgar Marples.

N-*N*-Dimethylsalicylamide is a stable substance; *N*-methyl-*N*-benzoylsalicylamide, however, is unstable, and under the conditions of its formation it is either instantly hydrolysed or rearranges, forming *N*-methyl-*O*-benzoylsalicylamide. It thus appears that, although derivatives of the general formula $C_6H_4<^{CO\cdot N\cdot R_2}_{OH}$ are stable, substances of the type $C_6H_4<^{CO\cdot N\cdot R\cdot Ac}_{OH}$ are too unstable to permit of isolation. This result is of considerable interest, since McConnan and Titherley have already shown (*Trans.*, 1906, **89**, 1327) that *N*-*N*-diacylsalicylamides, $OH\cdot C_6H_4\cdot CO\cdot N<^{R}_{R'}$, are too unstable to exist.

18. "The velocity of reaction of bromine with some unsaturated acids in aqueous solution." By Ernest Barrett and Arthur Lapworth.

Recent communications from W. Herz and B. Mylius (*Ber.*, 1906, **39**, 3816) and from J. J. Sudborough and J. Thomas (*Proc.*, 1906, **22**, 318) deal with the addition of bromine to cinnamic acid and its esters in organic solvents. We have been engaged in the examination of addition of bromine to some unsaturated acids in aqueous solutions in the hope of throwing some light on the mechanism of such reactions.

The changes are somewhat difficult to follow, as the velocities are very considerable, and even in dilute solutions the time must be measured in seconds instead of hours. The temperature employed was 14·9° in the first three cases and 25·5° with the monobromocinnamic acids, and the experiments were carried out in artificial light.

Cinnamic Acid.—With equimolecular proportions of acid and halogen in *N*/1000 solutions, nearly the whole of the bromine dis-

appeared in thirty seconds. With excess of bromine, 1·5 mols. were absorbed in about eighty minutes, this effect being due to the formation of bromocinnamic acids from the initial product. With crotonic acid and bromine, in equimolecular proportions in $N/200$ solutions, more than 9/10ths of the bromine was used in forty-five seconds.

Benzylidenemalonic Acid.—With $N/200$ solutions, about 0·5 mol. of bromine was absorbed in one minute, and the change had during the greater part of its course the form of a termolecular reaction. With the sodium salt the velocity is much greater, 9/10ths of the bromine disappearing in about thirty seconds. In $N/2$ sulphuric acid the velocity was about 1/10th of its usual value. Potassium bromide also lowers the reaction velocity, but not so decidedly; thus in $N/2$ potassium bromide the velocity was about 3/5ths of its ordinary value.

The reaction, towards its end, is complicated, the product losing hydrogen bromide and carbon dioxide, the resulting bromocinnamic acid accounting for some of the bromine. Thus with excess of bromine, $1\frac{1}{4}$ mols. of halogen disappeared in twenty minutes.

β-Monobromocinnamic Acid.—With equimolecular proportions of acid and bromine in $N/100$ solutions, about 0·25 mol. of bromine disappeared during the first half-minute. The change, in presence of excess of hydrogen chloride or potassium chloride, is of the bimolecular form; in absence of these agents the decomposition of the initial addition product occurs with measurable speed. The sodium salt is brominated at about the same rate as the free acid at first, but later the secondary reactions are more evident. Hydrogen chloride or potassium bromide diminish the reaction velocity, but apparently never to more than half the normal value. In this case, mineral acids have considerably less effect than have bromides, an observation consistent with the fact that the sodium salt and the acid have nearly the same velocity of bromination. The sodium salt of the stereoisomeric *α-monobromocinnamic acid*, it is interesting to note, absorbs bromine many times more rapidly than does the free acid.

The results appear inconsistent with the view that bromine dissociates into ions before addition at a double linking. They seem to show, however, that the ions of the acids, as well as the acids themselves, unite with bromine directly.

19. "Note on the molecular complexity of liquids." By Albert Ernest Dunstan and Ferdinand Bernard Thole.

In a recent paper (*Trans.*, 1906, **89**, 1774) Holmes deals with the question of molecular complexity from the point of view of the volume changes produced on mixing. By calculating the greatest difference between the volume of alcohol actually present and the volume

which would be present assuming no contraction, he assumes, for mixtures of alcohol and water, for example, that this maximum ($1C_2H_5{\cdot}OH,1H_2O$) implies approximation of the ratio of the radii of "influential spheres" to unity.

The following table shows that the ratio does not approximate to unity, taking as a basis of calculation the true molecular volumes given by the author:

	Mol. vol.	Max. difference of alcohol percentages by vol. at:	Above ratio of radii.
Ethyl alcohol	3·22	$C_2H_5{\cdot}OH,1\frac{1}{4}H_2O$	$\sqrt[3]{\frac{3{\cdot}22}{1}} = 1{\cdot}47.$
n-Propyl alcohol ...	4·07	$C_3H_7{\cdot}OH,1\frac{1}{2}H_2O$	$\sqrt[3]{\frac{4{\cdot}07}{1}} = 1{\cdot}60.$
Propionic acid	4·06	$C_2H_5{\cdot}CO_2H,1H_2O$	$\sqrt[3]{\frac{4{\cdot}06}{1}} = 1{\cdot}59.$
n-Butyric acid	5·08	$C_3H_7{\cdot}CO_2H,1H_2O$	$\sqrt[3]{\frac{5{\cdot}08}{1}} = 1{\cdot}72.$

Throughout the paper the author refers to the one constituent of a mixture as possessing the more active molecule usually of greater molecular volume and carrying a preponderating effect into the mixture. It would be more correct to look upon solution from the point of view of the reciprocal effect of the one component on the other; when this is done, for example, in the case of alcohol and water, the maximum effects are to be noticed at the proportions $1C_2H_5{\cdot}OH,3H_2O$ (Dunstan, *Trans.*, 1904, **85**, 823).

Holmes regards the lower alcohols and acids of the paraffin series, from similar considerations, as having the same complexity as water; water he assumes to have the aggregate formula $(H_2O)_2$. Now there is a considerable amount of evidence available which shows that the earlier liquids of homologous series tend to associate somewhat particularly those the members of which are hydroxylated.

It has been shown that the quantity $\frac{\text{Viscosity}}{\text{Mol. vol.}} \times 10^6$ is nearly constant, viz.: 60 for such liquids as are currently accepted as unimolecular, but for the hydroxylated associated class the values are much in excess of 60 (Dunstan, *Zeit. physikal. Chem.*, 1905, **51**, 732):

Benzene 65	Water 493	Acetic acid... 195
Chloroform 67	Methyl alcohol 138	Glycerol..... 106,000
Carbon disulphide... 60	Ethyl alcohol ... 189	

Again, when viscosity coefficients are plotted against molecular weights, not only do the alcohols and acids relatively stand apart from the unimolecular liquids, but also the curves show such

divergences at the beginnings of the series as to justify the idea of increased association.

Glycerol and nicotine are the only unimolecular liquids quoted in the table (p. 1785); now glycerol is not only notably viscous, but also has a remarkably high temperature coefficient of viscosity; both these facts indicate its association.

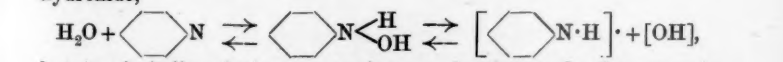
Carbon disulphide (*loc. cit.*) is mentioned as possessing four times the complexity of alcohol and is therefore represented by the formula $[CS_2]_8$; it is inconceivable from such data as, for example, its low boiling point, its low viscosity coefficient, the variation of its molecular surface energy with temperature, and its position in the molecular weight-viscosity chart.

Pyridine is quoted as a liquid which has the same molecular complexity as water and the alcohols. If this is so it is extraordinary that the viscosity concentration curves of mixtures of pyridine with alcohol on the one hand and with water on the other should be so entirely different. From an investigation now in progress on pyridine solutions it is found that in aqueous solution a maximum occurs at the proportions $2C_5H_5N,5H_2O$, and secondary irregularities at

$$3C_5H_5N,2H_2O,$$

$$2C_5H_5N,7H_2O,\ 1C_5H_5N,5H_2O,\text{ and }1C_5H_5N,10H_2O.$$

These discontinuities can only be explained by the assumption of loosely held complexes in dynamic equilibrium, which ionise to a considerable extent, and which generally behave like ammonium hydroxide,



but in alcoholic solution no maximum point is noted; the curve is composed of two branches which represent (1) the viscosity curve of associated alcohol with dissociated pyridine, and (2) dissociated alcohol with associated pyridine.

A precisely similar curve is afforded by alcohol–benzene mixtures. A study of the viscosity curves (Dunstan, *Trans.*, 1905, **87**, 11, and *loc. cit.*) enables the changes in association which take place to be followed qualitatively, whilst the curves connecting molecular weight with viscosity coefficient give a quantitative idea as to the degree of association existing in any given liquid.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Gibbs, *J. Willard.* The scientific papers of J. Willard Gibbs. (Edited by *Henry Andrews* **Bumstead** and *Ralph Gibbs van* **Name**.) 2 vols. pp. xxviii + 434, ix + 284. London 1906. (*Recd.* 3/1/7.)
From the Publishers: Messrs. Longmans, Green & Co.

Japp, *Francis Robert* and **Maitland,** *William,* **Knox,** *Joseph,* **Wood,** *James.* Researches in organic chemistry carried out in the University of Aberdeen. pp. iv + 86. Aberdeen 1905. (*Recd.* 15/1/7.)
From the University of Aberdeen.

Meldrum, *Andrew N.* Avogadro and Dalton. The standing in chemistry of their hypotheses. With a preface by *Francis R.* **Japp.** pp. viii + 113. Aberdeen 1904. (*Recd.* 15/1/7.)
From the University of Aberdeen.

Meyer, *Ernst von.* A history of chemistry from earliest times to the present day, being also an introduction to the study of the science. Translated by *George* **McGowan.** Third English edition. pp. xxvii + 691. London 1906. (*Recd.* 10/1/7.) From Dr. George McGowan.

Thresh, *John C.* and **Porter,** *Arthur E.* Preservatives in food and food examination. pp. xv + 484. ill. London 1906. (*Recd.* 29/12/6.)
From Dr. J. C. Thresh.

Vicarey, *R. W.* The treatment of storage batteries. pp. xi + 58. ill. London 1907. (*Recd.* 12/1/7.) From the Author.

II. *By Purchase.*

Dowson, *J. Emerson,* and **Larter,** *A. T.* Producer gas. pp. xiv + 295. ill. London 1906. (*Recd.* 9/1/7.)

III. *Pamphlets.*

Caldwell, *Robert J.* The hydrolysis of sugars. [A paper read before the York Meeting of the British Association, 1906.] pp. 26.

Crompton, *Holland.* Some molecular and latent heats. pp. 12. Salcombe 1906.

Finlow, *R. S.* The extension of jute cultivation in India. (From the *Bull. Agricultural Research Inst., Pusa,* 1906.)

Hughes, *Frank.* The occurrence of sodium salts in Egypt. With special reference to nitrate of soda. (From the *Yearbook, Khedivial Agric. Soc., Cairo.* 1905.)

ANNIVERSARY DINNER.

It has been decided by the Council to arrange for a Dinner of the Fellows of the Society and their friends on Friday, March 22nd, 1907, this being the day fixed for the Annual General Meeting. Further particulars will be announced shortly.

At the next Ordinary Meeting on **Thursday**, February **7th**, 1907, the following papers will be communicated:

"The rapid electro-analytical deposition and separation of metals. Part I. The metals of the silver and copper groups and zinc." By Henry Julius Salomon Sand.

"The alkaloids of ergot." By G. Barger and F. H. Carr.

"Influence of substitution on the formation of diazoamines and aminoazo-compounds. Part VI. The partially methylated 4 : 6-diamino-*m*-xylenes." By G. T. Morgan and F. M. G. Micklethwait.

"The reduction of hydroxylaminodihydroumbelluloneoxime." By F. Tutin.

"The constitution of umbellulone. Part II. The reduction of umbellulonic acid." By F. Tutin.

"Studies on optically active carbimides. Part V. The aryl esters and the amides of *l*-menthylcarbamic acid." By R. H. Pickard and W. Oswald.

"Some constituents of natural indigo. Part. I." By A. G. Perkin and W. P. Bloxam.

"The occurrence of isatin in some samples of Java indigo." By A. G. Perkin.

"On the absorption spectra of benzoic acid, the benzoates, and benzamide." By W. N. Hartley and E. P. Hedley.

"The absorption spectra of phthalic, *iso*phthalic, and terephthalic acids. Phthalic anhydride and phthalimide." By W. N. Hartley and E. P. Hedley.

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Issued 15/2/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 320.

Thursday, February 7th, 1907, at 8.30 p.m., Professor R. MELDOLA, F.R.S., President, in the Chair.

Mr. H. S. Redgrove was formally admitted a Fellow of the Society.

The PRESIDENT gave expression to the deep sense of loss experienced by Fellows of the Society through the death, on February 2nd, of Professor Dmitri Ivanovitsch Mendeléeff, F.R.S., and of Professor Nicolai Menschutkin, which occurred on February 5th. These chemists were Honorary and Foreign Members of the Society, having been elected in 1883 and 1898 respectively.

Certificates were read for the first time in favour of Messrs.:

John Campbell Allan, 91, Norse Road, Scotstoun, Glasgow.
Francis James Bailey, Findon Hill, Sacriston, Durham.
Charles Stanley Gibson, B.A., 45, Shakespeare Street, Manchester.
Joshua Craven Gregory, B.Sc., F.I.C., 126, Woodlands Road, Glasgow.
John Robinson, Agricultural College, Aspatria, Cumberland.

Of the following papers, those marked * were read :

***20. "The rapid electro-analytical deposition and separation of metals. Part I. The metals of the silver and copper groups and zinc." By Henry Julius Salomon Sand.**

The experiments on a new electro-analytical method of rapid determination and separation of metals referred to in a preliminary note (*Proc.*, 1906, 22, 43) have been continued. The metals hitherto studied are silver, mercury, copper, bismuth, lead, cadmium, and zinc. With the exception of the separation silver–mercury, each metal has been successfully separated from all the others by the method of graded potential. In order to separate silver from mercury the metals were deposited together, converted into their cyanides, and these separated in the usual way by means of their different behaviour to acids. The silver was then estimated electrolytically in the pure silver cyanide obtained. Experiments have been carried out in which the seven metals studied have been quantitatively separated from one solution. The silver was separated from the mercury as described above, and the lead and part of the bismuth were removed on the anode. All the other separations were brought about by graded potential. The metals were deposited in the following sequence. 1. Mercury and silver. 2. Lead and part of bismuth on anode ;—copper and rest of bismuth on cathode. 3. Cadmium. 4. Zinc. 5. After dissolving the combined deposit of copper and bismuth, the latter was estimated. 6. Rest of bismuth separated from lead after dissolving the deposit. 7. Lead. 8. Cadmium tested for traces of lead. One evaporation was necessary. The time required for the depositions in these experiments varied between five and fifteen minutes.

Discussion.

Mr. Edward Gardner asked if the author had had any experience in depositing copper from solutions containing a large quantity of ferric sulphate, and whether he had been able, in such solutions, to obtain an adherent deposit by any method of graded potential.

Mr. Sand stated that the presence of metals of variable valency, such as iron, which pass from one stage of oxidation to another with extreme readiness caused much difficulty. Work on such cases was being carried out at present.

*21. "The alkaloids of ergot."

By George Barger and Francis Howard Carr.

The authors assign to Tanret's crystalline ergotinine the formula $C_{35}H_{39}O_5N_5$, and have abandoned the formula $C_{28}H_{32}O_4N_4$ provisionally suggested in a preliminary note communicated to the British Association (*Chem. News*, 1906, **94**, 89). Tanret's original formula, $C_{35}H_{40}O_6N_4$, was based on faulty nitrogen determinations. In the above-mentioned note, the authors suggested the name ergotoxine for a second amorphous ergot alkaloid, of which they had crystallised several salts. Subsequently this alkaloid was described by Kraft (*Arch. Pharm.*, 1906, **244**, 336) as hydroergotinine, because by boiling its solution in methyl alcohol it was converted into ergotinine. Kraft did not analyse hydroergotinine.

In an attempt to acetylate ergotoxine with acetic anhydride the authors obtained ergotinine. As the latter alkaloid contains no acetyl group the change must be due to dehydration. The reverse change occurs when an ergotinine solution in dilute phosphoric acid is boiled. The crystalline phosphate of an amorphous alkaloid is then formed, closely resembling ergotoxine phosphate.

For ergotoxine the formula $C_{35}H_{41}O_6N_5$ is deduced from the analyses of the free base and of the following crystalline salts:
$C_{35}H_{41}O_6N_5,HCl$, m. p. 205°; $C_{35}H_{41}O_6N_5,H_3PO_4,H_2O$, m. p. 186—187°; $C_{35}H_{41}O_6N_5,C_2H_2O_4$, m. p. 179°, and $(C_{35}H_{41}O_6N_5)_2,C_2H_2O_4$, m. p. 179°.

The two formulæ, $C_{35}H_{39}O_5N_5$ and $C_{35}H_{41}O_6N_5$, thus independently arrived at for the crystalline and the amorphous alkaloid respectively establish the theory, first put forward by Kraft, that the former is the anhydride of the latter.

In contradistinction to ergotinine, ergotoxine is strongly active physiologically, producing all the typical effects of ergot. It is contained in most commercial specimens of ergotinine and also in Tanret's so-called "amorphous ergotinine."

Discussion.

Dr. Bywaters asked whether other alkaloids were known which passed from an inactive to an active form by being simply hydrated, and whether the fact of the active alkaloid being amorphous and forming a colloidal solution did not indicate that it was rather polymerisation instead of hydration that had occurred.

Dr. Barger stated that some alkaloids were known which behaved similarly to those mentioned in the paper. The salts of both alkaloids formed colloidal solutions under certain conditions.

*22. **"Influence of substitution on the formation of diazoamines and aminoazo-compounds. Part VI. The partially methylated 4 : 6-diamino-*m*-xylenes." By Gilbert Thomas Morgan and Frances Mary Gore Micklethwait.**

In examining the effect of substitution on the formation of *o*-aminoazo-compounds of the benzene series, the authors have methylated progressively 4 : 6-diamino-*m*-xylene and have studied the action of diazonium salts on the products. *Methyl*-4 : 6-*diamino*-m-*xylene* yields azo-derivatives like the unmethylated diamine itself, but as-*dimethyl*-4 : 6-*diamino*-m-*xylene* and *trimethyl*-4 : 6-*diamino*-m-*xylene* furnish stable diazoamines which are accompanied only by traces of azo-compounds.

Discussion.

The President congratulated Dr. Morgan on the extreme ingenuity of the method by which he had effected the progressive methylation of these substituted *meta*-diamines. He asked with reference to the possible formation of aminoazo-compounds with the azo- and dimethylamino-groups in the *ortho*-position whether the action of the usual transforming agents on the corresponding diazoamines had been tried, and if so with what result.

In reply to Dr. Cain's suggestion that steric hindrance might be the cause of the non-formation of azo-derivatives from tetramethyl-4 : 6-diamino-*m*-xylene, Dr. Morgan preferred to take the view that the absence of a labile hydrogen atom attached to nitrogen was the inhibiting factor. The non-formation of *ortho*azo-derivatives from tertiary amines was a general rule which held both in the benzene and naphthalene series, whereas the phenomena attributed to steric hindrance in one of these series were frequently not manifested in the other.

In reply to the President he stated that repeated attempts to transform the diazoamines of the *as*-dimethyl- and trimethyl-4 : 6-diamino-*m*-xylenes had not led to the isolation of definite aminoazo-compounds.

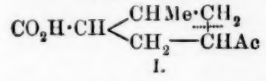
*23 **"The constitution of umbellulone. Part II. The reduction of umbellulonic acid." By Frank Tutin.**

When umbellulonic acid, $C_9H_{14}O_3$, obtained by the oxidation of umbellulone (*Trans.*, 1906, **89**, 1104), is reduced by means of sodium and alcohol, a *hydroxy-acid* having the formula $C_9H_{18}O_3$ is produced. It is evident from this fact that the ring contained in umbellulonic

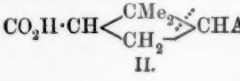
acid has been opened by the addition of two atoms of hydrogen, and the resulting hydroxy-acid must therefore be a chain compound.

This hydroxy-acid gives a *lactone* (b. p. 246—248°), and when oxidised with permanganate in presence of an excess of alkali yields acetic and *iso*propylsuccinic acids.

In the previous communication (*loc. cit.*) it was shown that umbellulonic acid must contain either a methylpentamethylene or a dimethyltetramethylene ring. Only two keto-acids containing either of these rings are capable of giving on reduction a hydroxy-acid, which, by subsequent oxidation, would yield acetic and *iso*propylsuccinic acids, namely, those possessing the following formulæ :



I.



II.

A hydroxy-acid which would yield on oxidation acetic and *iso*propylsuccinic acids, could only be formed from one of the above keto-acids by the opening of the ring on reduction at the place indicated by the dotted line. The product of the reduction of umbellulonic acid will therefore be *δ-hydroxy-α-*iso*propyl-*n*-hexoic acid*,

$$CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CH \cdot (CO_2H) \cdot CH(CH_3)_2.$$

Formula II represents pinononic acid, and it has previously been shown that umbellulonic acid is neither identical nor stereoisomeric with this compound. Umbellulonic acid must, therefore, be correctly represented by formula I.

It follows from this that the correctness of the formula previously assigned to umbellulone cannot be doubted.

*24. "The reduction of hydroxylaminodihydroumbelluloneoxime." By Frank Tutin.

Hydroxylaminodihydroumbelluloneoxime was prepared by Power and Lees in their investigation of the essential oil of *Umbellularia Californica* (*Trans.*, 1904, **85**, 636). When reduced with sodium and alcohol it gives a *base* (b. p. 136—138°/50 mm.), which is a liquid soluble in water. From the results obtained by the analysis of the *dibenzoate*, *dihydrochloride*, and *dibenzoyl* derivative of this base it is impossible to say with certainty whether it has the formula $C_{10}H_{20}N_2$ or $C_{10}H_{22}N_2$, although it is most probable that the latter is correct. The base may therefore be designated *aminotetrahydroumbellulylamine*.

Aminotetrahydroumbellulylamine dibenzoate crystallises in needles melting at 212—213°; the *dihydrochloride* also forms needles, but it is infusible at 305°. *Dibenzoylaminotetrahydroumbellulylamine* crystallises in prisms or in leaflets, which melt at 194°.

Although evidence was obtained of the presence of bases which are probably stereoisomeric with aminotetrahydroumbellulylamine, no derivative of them could be isolated in a state of purity.

25. "Studies on optically active carbimides. Part V. The aryl esters and the amides of *l*-menthylcarbamic acid." By Robert Howson Pickard and William Oswald Littlebury.

A continuation of the investigation of derivatives of menthylamine (see *Proc.*, 1905, **21**, 286). Eleven aryl esters and eighteen amides of *l*-menthylcarbamic acid were described and the rotations of these when dissolved in chloroform and pyridine compared. Attention was drawn to the approximately constant molecular rotation given by certain derivatives of menthylamine and menthol.

26. "Some constituents of natural indigo. Part I." By Arthur George Perkin and William Popplewell Bloxam.

Indigo-brown, an impurity of natural indigo, is best isolated by means of boiling pyridine. The crude product contains, in addition to small quantities of indirubin and a colourless wax, certain brown amorphous substances, of which the compound (*a*), $C_{16}H_{12}O_3N_2$, is present in by far the largest amount. This substance is insoluble in all the usual solvents except pyridine, but dissolves in alkali hydroxide solutions, and is readily reduced in this condition. When digested with strong aqueous potassium hydroxide it is converted into anthranilic acid and an amorphous, brown substance of uncertain composition. Two closely-allied compounds (*b*) and (*c*) present in but small amount have been isolated, the former of which is soluble in acetic acid and insoluble in alcohol, whereas the latter dissolves in alcohol. These substances, to which the respective compositions $C_{24}H_{22}O_5N_3$ and $C_{16}H_{14}O_4N_2$ are ascribed, closely resemble in general properties the compound $C_{16}H_{12}O_3N_2$, and from them also anthranilic acid was obtained. It is considered possible that these brown compounds are derivatives or condensation products of indoxyl, which are formed from indican during the process of manufacture. The leaves of the *Indigofera arrecta* and *I. Sumatrana* are practically devoid of tannin matter.

27. "The occurrence of isatin in some samples of Java indigo." By Arthur George Perkin.

During the examination of samples of Java indigo rich in indirubin, for yellow colouring matter (*Proc.*, 1904, **20**, 172) by extraction with

sodium carbonate solution and isolation of the products from the neutralised liquid with ether, there was obtained in addition to kampherol a small amount of substance crystallising from benzene in orange needles melting at 200°. This gave the thiophen reaction and was found to consist of isatin. The quantity present was exceedingly small, and in many other samples it appeared to be absent, but the point is interesting as it indicates that the formation of indirubin during the manufacture of natural indigo follows the well known synthesis of Baeyer (*Ber.*, 1881, **14**, 1745). Indirubin appears to be most readily formed when the fermented plant extract is oxidised under slightly alkaline conditions, and in these circumstances the oxidation of a portion of the indoxyl to isatin would appear to be facilitated.

28. "The absorption spectra of benzoic acid, the benzoates, and benzamide." By Walter Noel Hartley and Edgar Percy Hedley.

The absorption spectra of benzoic acid and phthalic acid were photographed by Hartley and Huntington, and characteristic bands were found in both; those of the former being situated between λ 280 and λ 270 with a continuous absorption beyond λ 255.

In a paper by Baly and Collie (*Trans.*, 1905, **87**, 1332) it is stated that "The spectrum of benzoic acid has been observed by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 257) and only shows general absorption rather strongly. This is only to be expected from the presence of the ketonic oxygen in the β-position."

As many benzoyl derivatives show absorption bands in their spectra, including benzaldehyde, it was considered necessary to settle this question decisively.

The absorption curves of benzoic acid, potassium and silver benzoates, and benzamide have been drawn from the photographs of the spectra of these substances, which were specially prepared and were of great purity and finely crystallised. The absorption bands of the different substances are all obviously related to the bands in benzoic acid, and the absorption is due to the benzene ring.

29. "The absorption spectra of phthalic, *iso*phthalic, and terephthalic acids, phthalic anhydride, and phthalimide." By Walter Noel Hartley and Edgar Percy Hedley.

Phthalic acid was examined by Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 257), but the isomeric acids have not been investigated. The sparing solubility of terephthalic acid rendered it necessary for its examination to convert it into the dimethyl ester and

to examine salts of the acid. It was found that phthalic anhydride, dissolved in cold alcohol, gave no absorption band, but that after warming for five minutes the spectrum showed a marked extension, and finally a strong absorption band was developed.

Phthalimide underwent no such change; it is therefore apparent that the group $\begin{matrix}CO\\CO\end{matrix}>NH$ is more stable than $\begin{matrix}CO\\CO\end{matrix}>O$.

o-Phthalic acid gives an absorption curve of the character that might be expected from a comparison with that of benzoic acid and from the difference in constitution between the two.

*iso*Phthalic acid has a shallow band of absorption situated in the same position as that of phthalic acid, but it is much less persistent.

Terephthalic acid being insoluble, its dimethyl ester and salts were examined, and it was found that the acid has no band, but merely an extension at or near where a band might be expected.

30. "$\alpha\alpha\gamma$-Trimethyl- and $\alpha\alpha\gamma\gamma$-tetramethyl-tricarballylic acids and $\alpha\delta$-dimethylbutane-$\alpha\beta\delta$-tricarboxylic acid." By Herbert Henstock and Charles Henry Graham Sprankling.

In a former communication by Bone and Sprankling, a method was given for the preparation of alkyl tricarballylic acids in alcoholic solution; in the case of the acids here discussed, the method has been modified and toluene was used instead of alcohol. The two reactions, (1) the condensation of the sodium compound of β-methylcyanosuccinic diethyl ester with α-bromo*iso*butyric ethyl ester, and (2) the condensation of the sodium compound of $\beta\beta$-dimethylcyanosuccinic diethyl ester with α-bromopropionic ester, should both yield products from which, on hydrolysis, $\alpha\alpha\gamma$-trimethyltricarballylic acid should be obtained. It was found, however, that in reaction (1) $\alpha\delta$-dimethylbutane-$\alpha\beta\delta$-tricarboxylic acid is produced; probably hydrogen bromide is first eliminated from α-bromo*iso*butyric ester, and the resulting methylacrylic ester condenses with the sodium compound of β-methylcyanosuccinic ester as follows: $CO_2Et\cdot CHMe\cdot CNa(CN)\cdot CO_2Et + CH_2{:}CMe\cdot CO_2Et = CO_2Et\cdot CHMe\cdot C(CN)(CO_2Et)\cdot CH_2\cdot CMeNa\cdot CO_2Et$. Reaction (2) yields $\alpha\alpha\gamma$-trimethyltricarballylic acid.

The condensation of $\beta\beta$-dimethylsodiocyanosuccinic diethyl ester with α-bromo*iso*butyric ester furnishes a product which, on hydrolysis, yields $\alpha\alpha\gamma\gamma$-tetramethyltricarballylic acid.

31. "A reaction of certain colouring matters of the oxazine series." By Jocelyn Field Thorpe.

Those colouring matters of the oxazine series which are derivatives of phenonaphthoxazine containing amino- or substituted amino-groups

in the position 6 of the phenonaphthoxazine ring, are readily converted into the corresponding phenonaphthoxazone by warming on the water-bath in the presence of very dilute acids. Thus Nile-blue A (3-diethylamino-6-aminophenonaphthoxazine sulphate) and Nile-blue 2B (3-diethylamino-6-benzylaminophenonaphthoxazine chloride) are converted into 3-diethylaminophenonaphthoxazone, melting at 204°, whereas New Methylene-blue GG (3:6-tetramethyldiaminophenonaphthoxazine chloride) and New Blue B (3-dimethylamino-6-dimethylaminophenylaminophenonaphthoxazine chloride) are converted into 3-dimethylaminophenonaphthoxazone, melting at 244°. Also those compounds which contain no substituting group in the position 6 in the phenonaphthoxazine molecule pass on warming with dilute acids into the corresponding oxazones containing the oxygen in that position. Thus, Meldola's blue (3-dimethylaminophenonaphthoxazine chloride) passes into 3-dimethylphenonaphthoxazone, melting at 244°, identical with the compound derived from New Methylene-blue GG and New Blue B.

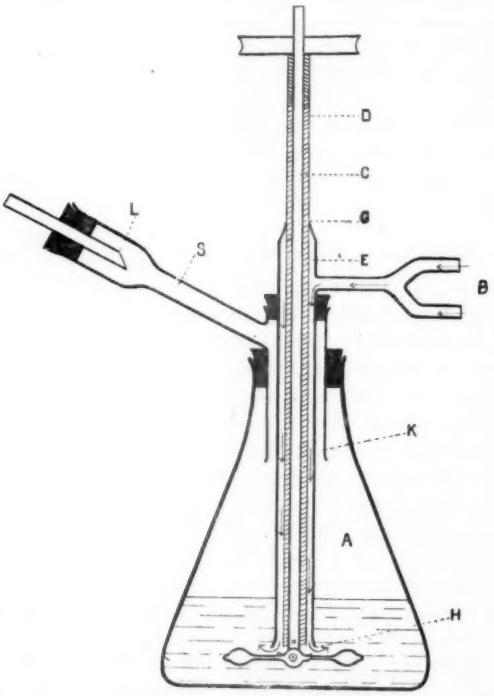
32. "The alkylation of *d*-fructose." By Thomas Purdie and David McLaren Paul.

The object of this research was to ascertain if ketoses can be alkylated by the methods already applied to aldoses, and to study the optical activity of the ketose derivatives thus obtained. Fischer's methylfructoside was methylated by means of methyl iodide and silver oxide. The resultant liquid, which had the composition of tetramethyl methylfructoside, gave on hydrolysis a liquid having the composition of tetramethyl fructose, and the properties of a reducing sugar. On realkylation, both by the silver oxide process and by Fischer's method, the substance yielded fully methylated methylfructosides. The rotatory powers of the series of compounds were abnormally low compared with that of the parent sugar. This anomaly, however, was finally explained by the isolation from the syrupy ketose of crystalline tetramethyl-α-fructose (m. p. 98—99°), which showed in alcoholic solution $[\alpha]_D^{20} - 94{\cdot}2° \longrightarrow -86{\cdot}7°$. After fusion, the substance exhibits mutarotation in the opposite sense, owing to partial transformation of the α-sugar into the β-form. This compound gave liquid tetramethyl methylfructosides of high rotatory power. Evidence was obtained that the low rotatory power of the syrupy ketose was probably due to the presence of an isomeric dextrorotatory hexose, produced by isomeric change during the preparation of Fischer's methylfructoside. Evidence was also adduced for the existence of two stereoisomeric fructosides in the latter substance.

33. "A simple apparatus, with stirrer, for treating a liquid at its boiling point with two or more gases." By Norman Leslie Gebhard.

Whilst studying the action of certain gases on liquids at their boiling points, the apparatus represented in the figure was devised and found very satisfactory.

The liquid is placed in an Erlenmeyer flask *A*, of capacity appropriate



to the volume of liquid under treatment. The rest of the apparatus includes a centrifugal stirrer in the liquid, driven by a water turbine through a horizontal pulley, the rod *C* carrying the stirrer rotating in an outer tube *D*. At *G*, *D* is sealed into a tube *E*, of slightly wider bore. The tube *E* reaches almost to the stirrer and dips well below the surface of the liquid. The gases enter at the tubes *B*, pass along the annular space between *D* and *E*, as indicated by the arrows, and encounter the liquid at *H* just above the stirrer. The upper part of *E*

is surrounded for part of its length by a wider tube *K* with a side tube *S*, through which the vapour of the boiling liquid passes to be condensed in the reflux condenser *L*. *E* is fitted to *K* and the latter to the flask by means of suitable corks. The apparatus enables a liquid, in vigorous ebullition, to be subjected to the action of gases, with constant stirring, and can be constructed without difficulty by anyone with a moderate knowledge of glass-blowing.

34. "Note on the arsenates of lead and calcium." By Spencer Pickering.

Crystallised sodium arsenate of commerce consists of the disodium salt, generally united with 7, but sometimes with 12, molecules of water of crystallisation. In either case, this water may all be expelled at 100°, and decomposition into the pyro-arsenate commences at 150°. The preparations dried at 300° in accordance with the Pharmacopœia are, therefore, overheated. With lead acetate, all commercially pure samples give a precipitate of triplumbic arsenate; but with lead nitrate, the precipitate consists of the diplumbic salt, mixed, occasionally, with a certain amount of the tri- or mono-plumbic arsenates. With preparations of crude sodium arsenate, the amount of lead salt required for precipitation varies considerably, and there is an indication that a compound of the di- and tri-plumbic salts may sometimes be formed.

With calcium chloride or nitrate, sodium arsenate forms the tricalcium arsenate; but, when thus prepared, it is not very insoluble, and is, therefore, unsuitable as an insecticide. But it may be completely precipitated by calcium hydroxide; and thus a mixture of lime and sodium arsenate may be used as a substitute for lead arsenate.

35. "Camphor-β-sulphinic acid and camphorylsulphonium bases." By Samuel Smiles and Thomas Percy Hilditch.

Camphor-β-sulphinic acid has been prepared by the reduction with zinc dust of the chloride of Reychler's camphorsulphonic acid. It was further shown that the acid when mixed with a phenolic ether and a dehydrating agent behaves in a similar manner to the aromatic sulphinic acids and yields the camphoryl sulphonium bases. The sulphinic acid and those sulphonium bases which have been prepared exhibit a strong lævorotatory power in distinction from the dextrorotatory sulphonic acid from which they were obtained. With the object of ascertaining whether this change in rotatory power is due to any alteration in structure of the camphor complex, the sulphinic acid was oxidised and and it was found that the products were the original sulphonic acid

and *d*-camphoryl-a-disulphone. The authors conclude that the above change is probably caused by the conversion of the sulphur from the sexavalent to the quadrivalent state.

36. "The condensation of salicylamide with aryl aldehydes." By Charles Alexander Keane and William Walter Scott Nicholls.

Benzaldehyde, when heated with salicylamide in presence of hydrochloric acid or of sodium acetate, condenses to form a cyclic compound, in the production of which one molecular proportion of the amide reacts with one of the aldehyde. The substance gives no coloration with ferric chloride, indicating that the hydroxyl group of the salicylamide has participated in the condensation, and it yields an acetyl derivative which is decomposed by concentrated sulphuric acid with the formation of *N*-acetylsalicylamide. It is accordingly regarded as a cyclic compound of the oxazine group, namely, 2-*phenyl*-1 : 3-*benzoxazone*, $C_6H_4<\begin{matrix}CO\cdot NH\\ O-CHPh\end{matrix}$; an alternative tautomeric formula is of course also possible. It crystallises from alcohol in silky needles which melt at 169°. On prolonged boiling with water it is gradually decomposed into its constituents; this decomposition is very readily effected by alkalis, less readily by dilute mineral acids. Heated with aniline, benzylideneaniline and salicylamide are formed. The *acetyl* derivative crystallises from alcohol in slender prisms which melt at 88°. It is decomposed into its constituents by heating with dilute alkalis or with dilute mineral acids, and when heated with aniline forms acetanilide, benzylideneaniline, and salicylamide.

2-p-*Methoxyphenyl*-1 : 3-*benzoxazone*, $C_6H_4<\begin{matrix}CO\cdot NH\\ O-CH\cdot C_6H_4\cdot OMe\end{matrix}$, is prepared by the condensation of salicylamide with anisaldehyde. It melts at 166—167° and forms an *acetyl* derivative which melts at 91°, and resembles the corresponding phenyl compound in its chemical behaviour.

*Benzylidene*bis-o-*methoxybenzamide*, $C_6H_5\cdot CH:(NH\cdot CO\cdot C_6H_4\cdot OMe)_2$, prepared by the condensation of *o*-methoxybenzamide with benzaldehyde, is much more stable towards alkali than the above cyclic compounds, and is not acetylated by heating with acetic anhydride. It crystallises from alcohol in fine needles meltin at 156°.

37. "The condensation of diethylmalonamide with aldehydes." By Harry Burrows and Charles Alexander Keane.

Diethylmalonamide, when heated with benzaldehyde in presence of hydrochloric acid, condenses similarly to salicylamide (compare Keane

and Nicholls, preceding abstract) to form a cyclic compound of the pyrimidine group: 4:6-*diketo*-2-*phenyl*-5:5-*diethylhexahydropyrimidine*, $CHPh<^{NH\cdot CO}_{NH\cdot CO}>CEt_2$. It crystallises in prisms which melt at 262°; it is stable towards dilute mineral acids, but is decomposed by boiling with sodium hydroxide solution. Heated with acetic anhydride it forms a *diacetyl* derivative which melts at 147° and which is decomposed with elimination of the acetyl groups by treatment with concentrated sulphuric acid.

The corresponding *cinnamyl* compound melts at 241° and also forms a *diacetyl* derivative which melts at 125°.

Chloral-diethylmalonamide, $CEt_2(CO\cdot NH_2)_2,CCl_3\cdot CHO$, is prepared by condensing molecular proportions of diethylmalonamide and chloral hydrate with hydrochloric acid. It melts at 178° and is stable towards boiling water or hot dilute hydrochloric acid.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Métropole, at 6.30 for 7 o'clock, on **Friday, March 22nd, 1907** (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Friday, March 15th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the next Ordinary Meeting on Thursday, February 21st, 1907, there will be a ballot for the election of Fellows and the following papers will be communicated :

"The constitution of oxyazo-compounds." By W. B. Tuck.

"The influence of solvents on the rotation of optically active compounds. Part IX. A new general method for studying intramolecular change." By T. S. Patterson and A. McMillan.

"The reduction products of *o*- and *p*-dimethoxybenzoin." By J. C. Irvine and A. M. Moodie.

"Replacement of halogens by hydroxyl. I. The hydrolytic decomposition of hydrogen and sodium monochloroacetates by water and by alkali, and the influence of neutral salts on the reaction velocities." By G. Senter.

"The reaction of ammonium salts with the constituents of the soil." By A. D. Hall and C. T. Gimingham.

"Constituents of natural indigo. Part II. Indigo-yellow." By A. G. Perkin.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, February 21st, 1907.

Allen, Alfred Frederick,
35, Purrett Road, Plumstead, Woolwich, S.E.

Student. Three years' training in Chem. Lab. of University College, London, for the B.Sc. Exam. (Lond.). Honours in Chemistry. B.Sc. Hons. 1906.

W. Ramsay. N. T. M. Wilsmore.
J. Norman Collie. Edward C. Cyril Baly.
Samuel Smiles.

Bagley, George,
Wellington, New Zealand.

Chemist. Works manager for Young's Chemical Works, Wellington, New Zealand, and formerly for the Metropolitan Chemical Co., Wellington, N. Zealand. Joint author with Professor Easterfield of paper on "The Constitution of Abietic Acid," *Trans.*, 1904.

Thomas H. Easterfield. P. W. Robertson.
B. C. Aston. *J. S. Maclaurin.*
Percy B. Phipson.

Baker, Frank, B.Sc.,
St. John's School, Eton.

Research Student at University College. Three years Student in the Chemical Laboratory, University College, London.

William Ramsay. Samuel Smiles.
J. Norman Collie. Edward C. Cyril Baly,
N. T. M. Wilsmore.

Bassett, Henry, jun.,

London (26, Belitha Villas, Barnsbury, N.).

Demonstrator and Assistant Lecturer, University of Liverpool. B.Sc. (Lond.); Ph.D. (Munich); D. ès Sc. (Nancy); F.I.C. 1851 Exhibition Scholar, 1903—1905. Have published papers alone or in conjunction with others in *Trans. Chem. Soc.*; *Berichte*; *Bull. Soc. Chim.*; *Journal de chemie physique*, &c.

J. Campbell Brown. F. G. Donnan.
William Ramsay. A. W. Titherley.
J. Norman Collie.

Benton, Frank Stanley,

"Hurstead," Reigate.

Assistant to John Heron, Esq., F.I.C., F.C.S. Certificated Student of the City and Guilds Technical College, Finsbury.

R. Meldola. John Heron.
John Castell-Evans. *John C. Umney.*
David Howard.

Berry, Leslie Hamilton,

"Penshurst," Croham Park Avenue, S. Croydon.

Lecturer and Demonstrator, Chemical Dept., Finsbury Technical Coll., B.Sc. (Hons.) London. Associate of the Institute of Chemistry.

R. Meldola. Lester Reed.
John Castell-Evans. Samuel Smiles.
Edward W. Bealey.

Cart, John Trevor,

4, Simonside Terrace, Heaton, Newcastle-on-Tyne.

Chemist. B.Sc. (Lond.); A.I.C.; Pharmaceutical Chemist. Jacob Bell Scholar, 1902—03. Jun. demonstrator Practical Chemistry in Pharm. Soc. School, 1903—04, and demonstrator in Pharmaceutics, 1904—05. Chemist with Messrs. Hopkin and Williams, 1905—06. Now with Messrs. C. A. Parsons & Co., Heaton Works.

Arthur W. Crossley. W. Palmer Wynne.
Herbert Jackson. Harold Deane.
C. T. Bennett.

Christie, John,

Eton College, Windsor.

Schoolmaster. B.A., Natural Sciences Tripos, Pt. I., 1905. Studied Chemistry for 4 years at Cambridge.

H. J. H. Fenton. H. O. Jones.
W. J. Sell. F. W. Dootson.
F. E. E. Lamplough.

Clough, George William,

29, Oseney Crescent, N.W.

Lecturer, Birkbeck College, E.C. B.Sc. (Birm.). Author of paper entitled "Condensation of Benzophenone Chloride with α- and β-Naphthols" (*Trans.*, 1906, **89**, 771).

Percy F. Frankland. Alex. McKenzie.
C. F. Baker. Henry Wren.
G. Druce Lander.

Cook, Taylor,

20, Shiddridge Street, Parson's Green, S.W.

Student at Royal College of Science, 1903—06; B.Sc., A.R.C.S. At present engaged in teaching at the Royal College of Science.

William A. Tilden. G. T. Morgan.
M. O. Forster. James C. Philip.
H. E. Fierz.

Dall, Colin Ernest,

"Maisonette," Maybury Road, Woking.

Student. Three years at University College, London. B.Sc., London, 1906. Hons. Chemistry.

William Ramsay. Edward C. Cyril Baly.
J. Norman Collie. Samuel Smiles.
N. T. M. Wilsmore.

Davidson, Francis,

Dover Place, Ashford, Kent.

Brewer and Maltster. Well up in General and Analytical Chemistry, able to do all analyses required in brewing and malting.

A. J. Murphy. *B. E. R. Newlands.*
Basil P. Wigan. *Arthur R. Ling.*
Basil Wm. Valentin. *Geo. Patterson.*
Thomas FitzGibbon.

Denham, William Smith,

2, Kelvinside Terrace North, Glasgow.

Lecturer in Chemistry, Glasgow and West of Scotland Technical College. Fellow of the Institute of Chemistry; B.Sc. (Lond.).

G. G. Henderson. T. S. Patterson.
Thomas Gray. Charles E. Fawsitt.
Alexander Davidson, jr.

Dikshit, Mohan Nath Kedarnath,

21, Burlington Road, Bayswater, London, W.

Medical Practitioner. Graduate of the Bombay University (Medical Faculty). Lord Reay Lecturer, Grant Medical College, Bombay.

Tutor in Physiology (Experimental and Chemical), G. .M. College, Bombay. Veine Analyser to the Techno-chemical Laboratory, Bombay.

John Muter. Geo. A. Turner.
A. H. M. Muter. *James W. Epps.*
J. H. B. Wigginton.

Eastaugh, Frederick Alldis,

Forty Hill, Enfield, then Sydney University, New South Wales.

Metallurgist, engaged as Teacher. First Class Associateship of the Royal School of Mines in Metallurgy. First Class Inter. B.Sc., London. Formerly assistant to Mr. G. T. Holloway, Chemist to Edison Ore Milling Syndicate. Demonstrator at R. S. M., and appointed same in Assaying and Chemistry at Sydney University.

W. Gowland. William A. Tilden.
S. Herbert Cox. James C. Philip.
G. T. Morgan.

Farmer, John Edwin,

"Blelsoe," New Road, Mitcham Junction.

Analyst to the Sewage Farms Committees. Corporation of Croydon. Sixteen years' experience of Sewage Purification, over eight years of which in the above. Member of the Society of Chemical Industry, also Member of the Royal Sanitary Institute.

J. Carter Bell. A. W. Cowburn.
W. J. Dibdin. James Ashton.
Frank Scudder.

Fowles, George,

28, Weltje Road, Hammersmith, W.

Science Master. Assistant Chemistry Master, Latymer Upper School, Hammersmith, W., since 1902. Intermediate Science (London Univ.), Honours in Chemistry; reading in Honours Chemistry for final B.Sc.

Frank E. Weston. W. H. Ratcliffe.
H. R. Ellis. *C. T. Bennett.*
Geo. W. T. Horrod.

Foxell, Edward William Lanchester,

22, Grand Avenue, Muswell Hill, N.

Chemistry Student, University College, London. Two years at University College, London. B.Sc. (London). Demonstrator in Chemistry, Univ. Coll., London.

William Ramsay. Edward C. Cyril Baly.
J. Norman Collie. N. T. M. Wilsmore.
Samuel Smiles.

Fryer, Percival John,

27, Minster Road, Cricklewood, N.W.

Analytical Chemist. For 4½ years Assistant to Mr. A. W. Stokes, F.I.C., F.C.S., Public Analyst. For last 2½ years, Analytical Chemist to the Chiswick Soap and Polish Co., W.

Alf. W. Stokes. Frank E. Weston.
Cecil Revis. J. L. White.

Henry R. Ellis.

Gibson, William Howieson,

48, Lady Margaret Road, Kentish Town, N.W.

Research Student in Chemistry. Three years a Student at University College, London. Third Class Honours in Physics, Intermediate Science, London. First Class Honours in Chemistry, B.Sc., London, 1906. Demonstrator at University College, London.

William Ramsay. Samuel Smiles.
J. Norman Collie. N. T. M. Wilsmore.

R. W. Gray.

Godden, William,

Station Road (East), Canterbury.

Two years assisting in teaching at Simon Langton Schools, Canterbury. Three years as Student at the Royal College of Science. A.R.C.Sc.; B.Sc. (Lond.); First Honrs. At present doing Research work at the Royal College of Science.

William A. Tilden. G. T. Morgan.
M. O. Forster. Chapman Jones.
James C. Philip. H. E. Fierz.

Green, William Heber,

The University of Melbourne.

Lecturer and Demonstrator in Chemistry. B.Sc. and Dixson Scholar in March, 1898; Kernot Scholar in 1899. D.Sc. in April, 1905; Demonstrator in Chemical Laboratory since April, 1898. Papers: "The Oxidation of Cane-sugar by Aqueous Solutions of Potassium Permanganate," *Proc. Roy. Soc.*, Victoria (1899), Vol. XI., "Notes on the Iceland Star Method for the Standardization of Hydrochloric Acid," *Chem. News* (1903), **87**, pp. 5—8.

Orme Masson. Fred. W. Steel.
Charles Tilburn. D. Avery.

Bertram D. Steele.

Grieb, Christopher Maurice Walter,

33, Torrington Park, North Finchley, London, N.

Research Student in Chemistry. Three years a Student in the

Chemical Laboratories at University College, London. Second Class Honours in Chemistry, B.Sc. (London), 1906. Final A.I.C. in Mineral Chemistry, Jan. 1907 (at first entry).

William Ramsay. N. T. M. Wilsmore.
J. Norman Collie. R. W. Gray.
Samuel Smiles. Edward C. Cyril Baly.

Higham, Richard,

133, Mauldeth Road, Withington, Manchester.

Principal, Plymouth Grove Municipal Sch., Manchester. First Class Certifs. Adv. Theor. and Pract. Chemistry; Lecturer for ten years in Ely. and Adv. Theor. and Pract. Inorg. Chem. Attended Honours Courses in above subjects. Special Tutor in Chemistry and Mathematics for Matric., Inter., and Final Exams. in Science. First Class Trained Certificated Master, &c.

Alfred Nixon. John Allan.
R. L. Taylor. Jas. Grant.
F. S. Sinnatt.

Hooton, William Marrs,

Repton, Burton-on-Trent.

Chemistry Master, Repton School. M.A. (Oxon., 1st Class Honours, Natural Science). Has carried on research work under Mr. A. G. Vernon Harcourt (on Nitrogen Peroxide) and under Prof. Campbell Brown (on Margaric Acid). M.Sc. (L'pool Univ., 1st Class Honours, Chemistry). Assoc. Institute of Chemistry. Late Head of the Science Dept., Middlesbrough High School and Technical School, 1902—6. Chemistry Master, Repton School.

A. Vernon Harcourt. J. Campbell Brown.
A. W. Titherley. W. Collingwood Williams.
Andrea Angel.

Hoyten, William James,

37, Ravelstoke Road, Wimbledon Park, London, S.W.

Surgeon. M.R.C.S., Eng.; F.R.C.P., Lond.; F.R.G.S., F.Z.S. Medallist and 1st Class Certif. Honours Owen's Coll., Practical Chemistry. Serumtherapy of Carcinoma (orig. research), *British Med. Journal*. Action of the Thyroid Gland (orig. research), *British Med. Journal*.

E. A. Fasnacht. *Chas. Turner.*
Joseph Gaskell. *Charles Dreyfus.*
William McCleary. *Ernest Bentz.*

Hughes, Francis Townshend Cunynghame,

Calcutta or Bombay, India.

Major, Indian Army. Qualified in Chemistry and Metallurgy at the Royal College of Science, and in Assaying at the Royal Mint according to regulations laid down for Indian Assay Dept. At present, holds appointment of Dept. Assay Master, Calcutta Mint.

William A. Tilden. W. H. Merrett.
G. T. Morgan. *Chapman Jones.*
G. S. Newth.

Hussey, Arthur Vivian,

"Banthwaite," Belmont, Sutton, Surrey.

Research Student, Central Technical College; Inter. B.Sc. (Lond.), Hons. in Chemistry; A.C.G.I.

Henry E. Armstrong. William A. Davis.
Gerald T. Moody. William Robertson.
T. Martin Lowry. Edward Horton.

Jackson, Ernest Wilfrid,

65, Douglas Terrace, Middlesbro'.

Analytical Chemist. Premium pupil with J. E. Stead, Esq., F.R.S., &c., 1896—1900, in whose laboratory have occupied the position of chief assistant chemist since 1900. (Honours, City and Guilds' Exam., Iron and Steel.) Teacher of Iron and Steel Manufacture in Technical College.

J. E. Stead. E. H. Saniter.
H. Frankland. *J. Archyll Jones,*
C. H. Ridsdale. *J. W. Patterson.*

Jackson, Victor George,

21, Frankfurt Road, Herne Hill, S.E.

Analytical Chemist. Engaged in analytical chemistry.

H. B. Baker. Frank E. King.
A. H. Coote. *A. Angel.*
James Leicester.

Jennings, Sidney James,

367, Queen's Road, New Cross.

Teacher. Spent three years (Sept., 1901 to Sept., 1904) in University College, London (Analytical), Laboratory, under Sir William Ramsay. Passed B.Sc. (London) in 1904. (Chemistry was one of the subjects.)

William Ramsay. N. T. M. Wilsmore.
Edward C. Cyril Baly. E. Barrett.
Francis W. Storey.

King, Albert Theodore,

Church Hill, Horsell, Woking.

Student. Three years at University College, London; B.Sc. Lond.; First Class Honours in Chemistry.

William Ramsay. Edward C. Cyril Baly.
J. Norman Collie. Samuel Smiles.
N. T. M. Wilsmore.

Lunan, George,

50, Garscube Terrace, Murrayfield, Edinburgh.

Pharmaceutical Chemist, 20, Queensferry St., Edinburgh. Formerly Examiner to Pharmaceutical Society of Great Britain. Papers on following subjects: "Note on Commercial Hypophosphorous Acid," *P. J.*, vol. xvii., fol. 773, 3rd series, 1886–87; "Hypophosphorous Acid," *P. J.*, vol. xviii., fol. 872, 3rd series, 1887–88; "Syrupus Ferri Hypophosphites," *P. J.*, vol. xviii., fol. 872, 3rd series, 1887–88; "Purity of Commercial Samples of Dried Sulphate of Iron," *P. J.*, vol. xix., fol. 226, 3rd series, 1888–89; "Tinctura Quininæ Ammoniata," *P. J.*, vol. xix., fol. 436, 3rd series, 1888–90; "Granular Effervescent Preparations," *P. J.* [4], vol. viii., p. 141, 1899; "Glycerinum Acidi Borici," *P. J.* [4], vol. xviii., p. 7, 1904; Report on "Effervescent Granules" for the Pharmacopœia Committee of the General Medical Council, *P. J.* [4], vol. xxiii., fol. 665 *et. seq.*, 1906.

Leonard Dobbin. Peter MacEwan.
M. Carteighe. *Alex Crum Brown.*
Walter Hills. *Charles A. Hill.*

Martin, Joseph,

Coopers' Company's School, Bow.

Teacher of Chemistry, Science Department, Coopers' Company's School, Bow. Three years Student in Armstrong College, Newcastle. B.Sc. degree (Durham University) in Chemistry. Assistant in Chemistry Department, Coopers' Company's School, Bow.

P. Phillips Bedson. S. Hoare Collins.
F. C. Garrett. Harold E. Richardson.
Clarence Smith.

Matthews, Charles Pask,

6, Fortess Road, London, N.W.

Science Master. Bachelor of Science Honours, University of London. Works Chemist, Messrs. Hopkin & Williams, Hatton Garden, E.C.

Late Assistant Science Master, Technical Science and Art Schools, Tiverton, Devon.

A. E. Thomas. Horace Finnemore.
John C. Umney. W. H. C. Jemmett.
W. H. Mills. A. E. Dunstan.

Murgatroyd, Louis,

1, Carlton Drive, Heaton, Bradford.

Analytical Chemist. Practised for two years as Analytical Chemist (Sutcliffe and Murgatroyd). Pupil to Dr. Petraczek (Analytical and Consulting Chemist, Bradford) for two years. Student for two years in the Chemistry Department, Yorkshire College. Studied under Dr. Hieppe in the laboratories of Meister, Lucius, & Brüning, Hœchst, a/M.

C. Rawson. *Joshua Knowles.*
Ad. Liebmann. *William E. Kay.*
Thorpe Whitaker. *W. H. Pennington.*
William G. White.

Oberländer, Otto, Ph.D.,

Chamber of Commerce Buildings, Oxford Court, Cannon Street, E.C.

Consulting Chemist. Student at Heidelberg University and Karlsruhe (Polytechnicum). Assistant to Professor Noelting Mülhausen (Alsatia). Manufacturing Chemist in Bury, near Manchester.

J. C. Cain. Arthur G. Green.
Ad. Liebmann. J. Tcherniac.
R. W. Sindall.

Remfry, Frederic George Percy, B.A. (Camb.), D.Sc. (Geneva),

Sunnymead, Tenby, S. Wales.

Research Student at University of Manchester, now Chemist in Research Laboratory, Messrs. Burroughs, Wellcome & Co. Joint author of following papers: "Formation and Reactions of Imino-compounds," *Jour. Chem. Soc.*, 1904. "Uber fünf Quinaldinderivate," *Ber.*, 1905.

Harold B. Dixon. J. F. Thorpe.
W. H. Perkin, jun. H. A. D. Jowett.
Frank Lee Pyman.

Robertson, Robert,

9, Sewardstone Road, Waltham Abbey, Essex.

Research Chemist. M.A.; D.Sc. of St. Andrew's University.

Fellow of the Institute of Chemistry. In charge of the Laboratory, Royal Gunpowder Factory. Has prosecuted researches in explosives, of which are published: "On the Will Test for Nitrocellulose," *J.S.C.I.*, 1902, p. 819, and "On Purifying and Stabilising Guncotton," *J.S.C.I.*, 1906, p. 624.

Horatio Ballantyne. W. Rintoul.
W. T. Thomson. Sydney S. Napper.
William Barbour.

Salway, Arthur Henry,

15, Palmerston Road, Forest Gate, E.

Research Chemist. Ph.D. (Leipzig), B.Sc. (Lond.).

Published in the Transactions of the Chemical Society a conjoint paper with F. S. Kipping on "The Arrangement in Space of the Groups Combined with the Tervalent Nitrogen Atom."

Frederick B. Power. M. Barrowcliff.
A. C. O. Hann. Frank Tutin.
Harold Rogerson.

Schlienger, Charles,

Acadia House, 273, Camden Road, London, N.

Assistant Lecturer. Chemical Department, East Ham Technical College. B.Sc. (London). Late Demonstrator in the Chemical Dept., Birkbeck College, London, E.C.

A. E. Dunstan. W. H. Barker.
W. T. Clough. Alex. McKenzie.
H. Wren.

Sewell, William George,

27, Park Road, Wandsworth Common, S.W.

Science Teacher. Bachelor of Science (London). I have studied Chemistry for 15 years, and would like to keep in touch with the latest researches. I have done some research, and am about to devote the whole of my leisure in this direction.

A. Greeves. H. R. Ellis.
Frank E. Weston. Léon E. Walling.
W. H. Ratcliffe.

Shepheard, Frederick George,

9, Leinster Road, Rathmines, Co. Dublin.

Chemist. B.Sc. First Class Honours in Chemistry, University of London. Associate of the Royal College of Science, London. Engaged

in research in the laboratory of Messrs. Guinness and Co. Joint author with Prof. Tilden of two papers in the *Transactions*.

William A. Tilden. G. T. Morgan.
M. O. Forster. James C. Philip.
G. S. Newth.

Smith, Robert Low,

56, Genesta Road, Plumstead, S.E.

Analytical Chemist. Training in Chemistry at King's College, 1902—04. Now occupying position as chemist of Johnson and Phillips' Electrical Engineering and Cable Manufacturing Works.

W. H. Deering. R. J. Redding.
Oliver Trigger. H. Russell Pitt.
J. C. Aylan.

Templeton, William Sandilands, M.A., B.Sc.,

Colombo, Ceylon (after 20th October, 1906).

Professor of Physics at the Medical and Technical Colleges, Colombo, Ceylon (recently appointed). Studied Chemistry at Glasgow University under Prof. Ferguson and W. R. Lang, at Glasgow and West of Scotland Technical College under Prof. G. G. Henderson and M. Parker, and at the Royal College of Science, S. Kensington, under Prof. Tilden and Dr. M. O. Forster. Was a teacher of Chemistry for two years in Allan Glen's School, Glasgow. Desires to keep in touch with the latest developments of Chemical Science in view of his having occasionally to undertake the duties of the Prof. of Chemistry at Colombo.

F. E. Matthews. A. Campion.
John Ferguson. F. W. Harbord.
M. O. Forster.

Thomas, Richard Noel Garrod,

Balliol College, Oxford.

Bachelor of Arts. Demonstrator in Chemistry, Balliol Coll., Oxon. Part author of a paper on "Spontaneous Crystallisation" (*J.C.S.*, July, 1906).

Harold Hartley. N. V. Sidgwick.
D. H. Nagel. A. F. Walden.
W. W. Fisher.

Toch, Maximilian,

261, West 71 Street, New York City.

Chief Chemist and member of firm of Toch Brothers, Colour and Varnish Mfrs., N.Y. Graduate and Post Graduate, New York University. Graduate Chemical Department, Cooper Institute.

Author of "Chemistry of Mixed Paints," "Permanent Protection of Iron and Steel," "Composition of Paints and Raw Materials," &c.

Chas. Baskerville. Leo F. Guttmann.
F. P. Venable. Peter T. Austen.
James Lewis Howe. William Ramsay.

Chas. H. Herty.

Twiney, William George,

St. Joseph's College, Colombo, Ceylon.

Science Master. B.Sc., London; Third Class Honours Chemistry. Two years Science Master, Dorchester Grammar School. Science Master, St. Joseph's College, Colombo.

E. K. Hanson. J. W. Dodgson.
John W. Taylor. *J. K. H. Inglis.*

A. E. Bellars.

Watkins, Charles Rowlatt,

Aldenham School, Elstree, Herts.

A Science Master at Aldenham, now Assistant Collector in Imperial Customs Service, Madras, India. Formerly Scholar of Emmanuel Coll., Cambridge. Natural Science, Tripos I. and II.

G. D. Liveing. F. W. Dootson.
Charles T. Heycock. T. B. Wood.
W. J. Sell. H. O. Jones.

Wight, Robert Burt,

3, Clarendon Terrace, Linthorpe Road, Middlesbrough.

Teacher of Science. M.A., Cantab (Hons., Nat. Sci. Tripos), Inter. B.Sc. (Lond.). Head of Science Department, Middlesbrough. High School and Middlesbrough Technical Classes, late Head of Science Department, Oldham Hulme Grammar School.

J. E. Stead. *H. Frankland.*
J. Archyll Jones. *C. H. Kidsdale.*
J. W. Patterson. *E. H. Saniter.*

Williams, William Henry,

Government Education Department, Hong Kong.

1903—5, Supervisor Anglo-Chinese Schools; 1905—present, Headmaster Victoria School (Secondary School for Boys). Organizing Secretary to Govt. for Tech. Instruction. Student: three years Inorg. Chem.; two years Organic Chem., Municipal Tech. School, Birmingham. Board of Educ. Certifs., 1st Lond. Matric. (Chemistry). Author of "Experiments in Hygiene," a teacher's handbook for instruction in

Tropical Diseases and Sanitary Science, printed and published by the Hong Kong Government. Asst. Lec. (1900—1), Munic. Tech. Day School, B'gham; two years Lecturer in Chemistry and Physics, Institute of Engineers, Hong Kong.

Lionel M. Jones. *T. Slater Price.*
T. Francis Rutter. *Douglas F. Twiss.*
W. A. S. Calder. *J. A. Harrison.*

Wolff, Mark Arthur,

6, Hanover Terrace, Holland Park, W.

Assayer, Analytical Chemist, and Mining Engineer. For two years Chief Assayer and Advising Chemist to the Wei-Hai-Wei Gold Mining Company of Shanghai, China (July, 1904—September, 1906).

W. H. Merrett. J. W. Shepherd.
E. O. Courtman. *G. T. Morgan.*
J. C. Philip.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 321.

Thursday, February 21st, 1907, at 8.30 p.m., Professor R. MELDOLA, F.R.S., President, in the Chair.

Messrs. T. S. Patterson and E. G. Streimer were formally admitted Fellows of the Society.

The PRESIDENT announced that the Society had incurred a further loss by the death of Professor Henri Moissan, which occurred on February 20th, in Paris; the late Professor Moissan was elected an Honorary and Foreign Fellow Member of the Society on January 20th, 1898.

On behalf of the Executive Committee of the Coal Tar Colour Jubilee Celebration, it was stated by the Chairman, Professor R. Meldola, that the Council of the Society had that afternoon accepted the marble bust of Sir William Perkin, which was to be placed in the rooms of the Chemical Society according to the decision of the public meeting at which the celebration was inaugurated.

It was further stated that the Council had received and acknowledged, in the name of the Society, an important addition to the Research Fund in the form of a contribution of £1000 from the Worshipful Company of Goldsmiths.

Certificates were read for the first time in favour of Messrs.:

William Robert Ball, B.Sc., 48, Cambridge Road, Thornaby-on-Tees.
Alexander Thomas Cameron, M.A., B.Sc., Burtonhill, Malmesbury.

Geoffrey Dodleston Hope, B.Sc., Ph.D., Heath Heys, Oxton.
The Hon. Raymond Egerton Hubbard, Addington Manor, Winslow.
Herbert Brooke Perven Humphries, B.Sc., 117, Avenell Road, Highbury, N.
James McConnan, M.Sc., Ph.D., Danehurst, Greenbank Drive, Liverpool.
Percy Joseph Rhodes, Bridge House, Church.
Sydney William Smith, B.Sc., 76, Norroy Road, Putney, S.W.
Nicholas Tarr, Lucton School, Herefordshire.
William Scott Tebb, M.A., M.D., Sandfield, Putney Heath Lane, S.W.

It was announced that the following changes in the Officers and Council were proposed by the Council.

As President: Sir William Ramsay, K.C.B., F.R.S.; *vice*, Prof. R. Meldola, F.R.S.

As Foreign Secretary: Dr. Horace T. Brown, F.R.S.; *vice*, Sir W. Ramsay.

As Vice-Presidents: Prof. J. J. Dobbie, F.R.S., and Sir Alexander Pedler, F.R.S.; *vice*, Dr. H. T. Brown, F.R.S., and Prof. H. B. Dixon, F.R.S.

As Ordinary Members of Council: Mr. G. T. Beilby, Dr. W. R. Hodgkinson, Mr. E. Grant Hooper, and Dr. H. R. Le Sueur; *vice*, Prof. W. Gowland, Mr. A. D. Hall, Dr. A. Lapworth, and Mr. J. E. Marsh, F.R.S.

Mr. E. Grant Hooper, Dr. H. F. Morley, and Dr. H. R. Le Sueur were elected Auditors to audit the Society's accounts.

A ballot for the election of Fellows was held, and the following were declared duly elected:

Alfred Frederick Allen B.Sc.
George Bagley.
Frank Baker, B.Sc.
Henry Bassett, jun., B.Sc., Ph.D.
Frank Stanley Benton.
Leslie Hamilton Berry, B.Sc.
John Trevor Cart, B.Sc.
John Christie, B.A.
George William Clough, B.Sc.
Taylor Cook.
Colin Ernest Dall, B.Sc.
Francis Davidson.
William Smith Denham, B.Sc.
Mohan Nath Kedarnath Dikshit.
Frederick Alldis Eastaugh.
John Edwin Farmer.
George Fowles.
Edward William Lanchester Foxell, B.Sc.
Percival John Fryer.
William Howieson Gibson, B.Sc.
William Godden, B.Sc.
William Heber Green, D.Sc.
Christopher Maurice Walter Grieb, B.Sc.
Richard Higham.

William Marrs Hooton, M.A., M.Sc.
William James Hoyten, M.R.C.S. F.R.C.P.
Francis Townshend Cunynghame Hughes.
Arthur Vivian Hussey.
Ernest Wilfrid Jackson.
Victor George Jackson.
Sidney James Jennings, B.Sc.
Albert Theodore King, B.Sc.
George Lunan.
Joseph Martin, B.Sc.
Charles Pask Matthews, B.Sc.
Louis Murgatroyd.
Otto Oberländer, Ph.D.
Frederic George Percy Remfry, B.A., D.Sc.
Robert Robertson, M.A., D.Sc.
Arthur Henry Salway, Ph.D., B.Sc.
Charles Schlienger, B.Sc.
William George Sewell, B.Sc.
Frederick George Shepheard, B.Sc.
Robert Low Smith.
William Sandilands Templeton, M.A., B.Sc.
Richard Noel Garrod Thomas, B.A.
Maximilian Toch.
William George Twiney, B.Sc.
Charles Rowlatt Watkins, B.A.
Robert Burt Wight, M.A., B.Sc.
William Henry Williams.
Mark Arthur Wolff.

The Council has ordered the following report to be printed in the Proceedings of the Society:

RECOMMENDATIONS AS TO THE NOMENCLATURE OF THE PROTEINS.

It is well known that much confusion arises at the present time from the lack of any understanding, either here or abroad, as to the exact sense in which the various names applied to proteins (Proteinstoffe, Eiweisskörper, Albuminoids) and their derivatives shall be used. No little difficulty is created by the use of a term in different senses, as well as ambiguity of meaning in some cases. It appeared desirable, therefore, to lay down rules for the guidance of students and workers, at all events in this country, which would tend to promote some degree of uniformity of usage. It was obviously desirable to retain existing terms as far as possible, especially as it was clear that the time is not yet come to coin strictly systematic names and that only provisional recommendations are desirable in the existing state of knowledge.

The following report is the outcome of a prolonged consideration of the subject by a number of chemists and physiologists. The original Committee was called into being by the Physiological Society; its members were nominated by the two societies. The report of the Committee was subjected to criticism, both by the Physiological Society and by the Publication Committee of the Chemical Society. At the instance of the latter body a number of chemists specially interested in the subject then took the matter into consideration in conjunction with a few representatives of the

Physiological Society; finally, a draft report embodying the conclusions arrived at was prepared by Drs. Halliburton and Hopkins, which was considered and amended at a meeting of the Publication Committee of the Chemical Society, at which the physiologists were present.

RECOMMENDATIONS.

I. The word Proteid—which is used in different senses in this country and in Germany—should be abolished.

II. The word Protein is recommended as the general name of the whole group of substances under consideration. It is at present so used both in America and Germany. It admits readily of the use of such derived words as protease and proteose. If used at all, the term Albuminoid should be regarded as a synonym of protein.

III. The sub-classes should be as follows:—

1. Protamines. These are simple members of the group. They are exemplified by substances like salmine and sturine which have been separated from fish-sperm.

2. Histones. These are more complex substances: this and the previous class probably pass gradually into one another. The class is exemplified by the histones separated by Kossel from blood corpuscles; precipitability by ammonia is one of their distinguishing features.

3. Albumins. These are proteins of which egg-albumin and serum-albumin may be taken as typical examples.

4. Globulins. These are proteins which differ from the albumins in solubility; they are more readily "salted out" of solution than the albumins. They are exemplified by serum-globulin and fibrinogen. The class should also include certain derivatives of globulins such as fibrin and myosin.

N.B.—The carbohydrate radicle separable in small quantities from many members of Classes 3 and 4 is probably not to be considered as a prosthetic group, as it is in the gluco-proteins (see below).

N.B.—It appeared advisable, especially from the teachers' standpoint, to introduce a general term to include proteins coagulable by heat (Classes 3 and 4); but a term likely to meet with general acceptance has not yet been suggested.

5. Sclero-proteins. This new word takes the place of the word

albuminoid in the limited sense in which the majority of physiologists have been accustomed to use it. It includes such substances as gelatin and keratin; the prefix indicates the skeletal origin and often insoluble nature of its members.

6. Phospho-proteins. This class includes such substances as vitellin and caseinogen with its derivative casein. The prefix nucleo- frequently used in relation to this class is incorrect and misleading.

7. Conjugated proteins. These are substances in which the protein molecule is united to a "prosthetic group." The principal subdivisions are:—

a. Nucleo-proteins.

b. Gluco-proteins (*e.g.*, mucin).

c. Chromo-proteins (*e.g.*, hæmoglobin).

8. Derivatives of Proteins. Of these the products of protein-hydrolysis (a term preferable to proteolysis *) are those which require special attention. These should be classified as follows:—

a. Meta-proteins. This term is suggested in place of albuminate (acid-albumin, alkali-albumin), which is objectionable because (1) these products are obtainable from both albumins and globulins, also (2) because the termination ate implies a salt.

b. Proteoses. This term includes albumose, globulose, gelatose, &c. The subdivision of these into proto-, hetero-, deutero-proteoses, &c., and the various modifications of Kühne's original classification have been considered; the whole subject is, however, at present too unsettled for any final nomenclature of these subdivisions to be proposed.

c. Peptones. This term should be restricted to the further products of hydrolysis which differ from the proteoses inasmuch as they cannot be salted out from solution and usually resemble them in giving the biuret test.

N.B.—It has been pointed out that certain vegetable products hitherto regarded as peptones do not give the biuret test. It does not appear possible to bring such exceptional substances into any general classification at present. The same difficulty in classify-

* Although mindful of the unfortunate fact that terms such as proteolysis fail to convey a meaning in harmony with that which is conveyed by the terms electrolysis and hydrolysis (on which they are moulded) of decomposition *by*, the Committee have not ventured to deal with the difficulty; they recognise, however, that the practice is one to be obviated, if possible (compare Armstrong, *Proc. Roy. Soc.*, 1904, **73**, 500).

ing arises in connexion with certain other vegetable proteins; for instance, those which like gliadin are soluble in alcohol.

d. Polypeptides. The majority of the polypeptides are synthetical substances. Some, however, have been separated from the products of protein-hydrolysis and it is therefore advisable to include them in the present classification. They are products of cleavage beyond the peptone stage and consist of two or more amino-acids in association; the majority of those hitherto prepared do not give the biuret test.

IV. The term caseinogen should be used for the principal protein in milk and casein for its derivative which is the result of the action of rennet.

V. The two principal proteins of the muscle plasma should be termed paramyosinogen and myosinogen; the term soluble myosin should take the place of v. Fürth's soluble myogen-fibrin; the term myosin should be restricted to the final product formed during *rigor mortis*.

Of the following papers, those marked * were read:

*38. "The constitution of hydroxyazo-compounds." By William Bradshaw Tuck.

Several workers have proved that the ethers of all hydroxyazo-compounds and the benzoyl derivatives of the *p*-compounds possess the azo-structure, but that the benzoyl-*o*-hydroxyazo-compounds have the quinone-hydrazone configuration.

Chemical methods, however, have failed to produce a unanimous opinion with regard to the constitution of the free hydroxy-compounds.

As the absorption spectrum for azobenzene has been shown to be very different from that characteristic of quinones, several of the hydroxyazo-compounds were examined spectrographically.

The absorption spectra of the *p*-hydroxy-compounds agree extremely closely with those of their derivatives; further, hydrochloric acid produces the same very characteristic change in the spectra of the phenolic substances and their ethyl ethers. This proves that the constitution in the two cases is similar, that is, the free hydroxy-compounds are in the azo-form. The ethers of *o*-compounds also agree with the *p*-compounds, but the benzoyl derivatives are similar to benzoquinonebenzoylphenylhydrazone. The absorption spectra of all the azo-derivatives examined confirm the hypothesis previously put forward for the colour of azobenzene (*Trans.*, 1906, **89**, 982).

Discussion.

Dr. Hewitt agreed with Mr. Tuck that in the case of the *p*-hydroxyazo-compounds, the free substances, their ethers and esters were all of the azo-phenolic type, but was uncertain whether a solution of these substances in concentrated hydrochloric acid really contained much hydrochloride, since the bases being very weak, must have suffered considerable hydrolytic dissociation.

The contention that the *o*-hydroxyazo-compounds and their benzoyl derivatives corresponded to quinone-hydrazones was based apparently on the observation of Goldschmidt and Brubacher that acyl anilides result on complete reduction of the acyl derivatives of benzeneazo-*p*-cresol. This might, however, be equally well the result of a secondary reaction, since esters and primary amines normally react to give alcohols or phenols and acid amides. Against these equivocal results must be placed the positive evidence that on substitution these compounds behave as azophenols whether they belong to the para- or ortho-series.

The only other physical method hitherto adopted in the case of the hydroxyazo-compounds has been the application of cryoscopic determinations in non-hydroxylic solvents by Auwers and Orton, whose results indicate that the para-compounds are azophenols and give no positive result for the ortho-substances.

Goldschmidt himself abandoned the idea that the *o*-hydroxyazo-compounds were quinone-hydrazones, and his observation that the acylated compounds of both series reduce to hydrazo-compounds which are insoluble in alkali distinctly points to acylation, with respect to oxygen, having taken place.

Dr. Lowry said that Oddo's theory of "mesohydry" to which the author had referred was in many respects a reversion to Laar's theory of "tautomerism," since it postulated that a mobile hydrogen atom might be equally attached to oxygen and to nitrogen or carbon. If the hydrogen atom was capable under any conditions of settling in either of the alternative positions the phenomenon was not one of tautomerism, but a mere case of labile isomerism, which might become dynamic when the compound was liquefied with or without the addition of a catalyst. The separation of a single isomeride was a normal result of crystallisation, and, so far as he was aware, no genuine case of mesohydry or of tautomerism had yet been established. It was doubtful whether the hydrazo-compounds would prove to be an exception, although the possibility remained open that the crystals might, in certain cases, be isomorphous mixtures of two or more isomerides.

***39. "The influence of solvents on the rotation of optically active compounds. Part IX. A new general method for studying intramolecular change." By Thomas Stewart Patterson and Andrew McMillan.**

The influence of benz*anti*aldoxime as a solvent on the rotation of ethyl tartrate was found to be very remarkable. A method of studying intramolecular change was described which had been applied in the cases of benzaldoxime, anisaldoxime, and ethyl phenylformylacetate.

***40. "Displacement of halogens by hydroxyl. I. The hydrolytic decomposition of hydrogen and sodium monochloroacetates by water and by alkali, and the influence of neutral salts on the reaction velocities." By George Senter.**

By varying the initial concentration within fairly wide limits, it was shown that the hydrolytic decomposition of monochloroacetic acid by hot water according to the equation $CH_2Cl{\cdot}CO_2H + H_2O = OH{\cdot}CH_2{\cdot}CO_2H + HCl$ is strictly unimolecular up to $N/2$ solution; the reaction velocity is somewhat retarded by hydrochloric acid, but is not affected by sodium chloride. The conclusion is drawn that water and the undissociated acid are the reacting substances; if an intermediate compound is formed, it is the rate at which it breaks down into glycollic and hydrochloric acids which is measured.

The decomposition of sodium chloroacetate by water is strictly unimolecular in dilute solution, but in solutions more than 0·1 molar, the velocity increases more rapidly than the concentration. The reaction is retarded by neutral salts. Potassium and barium chloroacetates undergo decomposition at the same rate as the sodium salt.

The interaction of sodium chloroacetate and $N/10$ sodium hydroxide, according to the equation $CH_2Cl{\cdot}CO_2Na + NaOH = OH{\cdot}CH_2{\cdot}CO_2Na + NaCl$, proceeds only about ten times more rapidly than the corresponding change in aqueous solution under equivalent conditions. The reaction velocity in the presence of alkali is accelerated, and to the same extent, by such neutral salts as sodium chloride, sulphate, and nitrate in equivalent solution.

On the basis of these results and of the previous observations of Arrhenius, the hypothesis put forward by R. J. Caldwell (*Proc. Roy. Soc.*, 1906, *A*, 78, 272), according to which the accelerating influence of neutral salts on reactions in which acids (and alkalis) exert a catalytic action is ascribed to the withdrawal of water by the salt and conse-

quent concentration of the reacting substances, was criticised. It is considered that the effect in question is due to the action of the ions of the salt on H′ and OH′ ions.

Discussion.

Dr. Senter, replying to Dr. E. F. Armstrong, said that in his experiments, as in those of Arrhenius quoted in the paper, the ratio of alkali and acid respectively to water was constant, except for the slight differences in the amounts of water displaced by equivalent quantities of the neutral salts employed; that these differences did not amount to more than about 1 per cent. of the total volume, and were therefore negligible in comparison with the magnitude of the neutral salt effect. Moreover, it did not seem quite justifiable to conclude from the results of experiments with sucrose, the solution volume of which is large and remains unaltered on dilution, that solutions for comparison should in all cases be prepared by adding a definite weight of the solute to a definite weight or volume of the solvent (H. E. Armstrong, *Proc. Roy. Soc.*, 1906, **78**, *A*, 264); in particular, salts which in certain dilutions have a negative solution volume seem to present difficulties from this point of view.

***41. "The interaction of ammonium salts and the constituents of the soil." By Alfred Daniel Hall and Conrad Theodore Gimingham.**

As it has been observed that an acid reaction develops in soil which has been repeatedly manured with ammonium salts, the authors have re-examined the action of ammonium salts on the chief constituents of soil. Solutions of various strengths, N to $N/100$, of ammonium sulphate, chloride, or other salt were shaken for twenty-four hours with silica, clay, calcium carbonate, and humus respectively, and the composition of the resulting solution was determined.

With silica, there is no action. With clay, a double decomposition takes place between the ammonium salt and zeolitic bodies in the clay, ammonium being withdrawn from solution and replaced by equivalent quantities of calcium, magnesium, and potassium. With varying strengths the reaction can be represented by the equation

$$\frac{(\text{Ammonium withdrawn from solution})^2}{\text{Ammonium remaining in solution}} = \text{K},$$

as long as the clay is in excess. If the clay is not in excess, it can only take up a fixed amount of ammonium whatever the strength of the solution. No acid reaction is produced, and there is no adsorption of the salt as a whole.

With calcium carbonate, the reaction does not proceed far, and the extent may be represented by an equation of similar form. With natural humus from various sources, the reaction is similar to that with clay; other bases, chiefly calcium, are displaced by ammonium; there is no development of acidity and no adsorption.

The acid reaction observed in the field is thus not due to inorganic causes; a biological origin has been found.

42. "The reduction products of *o*- and *p*-dimethoxybenzoin." By James Colquhoun Irvine and Agnes Marion Moodie.

o-Dimethoxybenzoin has been converted into the corresponding hydrobenzoin, and the latter compound, when reduced by Baeyer's process, gives *p*-dimethyltolane. This abnormal change has been shown to take place through the intermediate formation of *o*-dimethoxydiphenylethylene together with the corresponding ethane derivative.

As this result indicates that Baeyer's method of reduction may lead to erroneous conclusions in deducing the constitution of aromatic alkyloxy-compounds, a detailed study of the effect of the process on derivatives of anisoin has been made. It has been shown that both anisoin and its methyl ether are converted into deoxyanisoin when distilled with zinc dust in a current of carbon dioxide, and that the reduction is only complete when carried out in an atmosphere of hydrogen. The hydrocarbon finally obtained was stilbene.

In the course of the work a number of new derivatives of anisoin were prepared and examined.

43. "Constituents of natural indigo. Part II." By Arthur George Perkin.

Preliminary accounts of a portion of this work have previously appeared (*Proc.*, 1904, 20, 172, and *ibid.*, 1906, 22, 199). The kaempferol glucoside, kaempferitrin contained in the *Indigofera arrecta* is not hydrolysed by the insoluble indigo enzyme of Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, 120), and its appearance in Java indigo is probably due to some extent to the employment of sulphuric acid at one stage of the manufacture. Numerous Java indigos have been examined, and all contained kaempferol, but in no case did this exceed 0·2 per cent. The leaves of the *Indigofera sumatrana* contain a trace of yellow colouring matter which probably consists of kaempferol.

44. "The velocity of hydrolysis of aliphatic amides." By James Codrington Crocker.

The rates of reaction of formamide, acetamide, propionamide, butyramide, *iso*butyramide, valeramide, capronamide with hydrochloric acid have been determined at from 40° to 80°. The determinations were carried out by measurement of the specific conductivity of the reacting mixture. Owing to the effect of the dissolved amide on the conductivity of the solution, the concentration could not be calculated directly from the specific conductivity. Synthetical mixtures were prepared representing definite stages of the reaction, and the variation of the specific conductivity of these with time was determined. By extrapolation to $t = 0$ the initial specific conductivity was determined in each case. A concentration-conductivity curve was plotted which served to standardise the original conductivity-time curve. The reactions are bimolecular and follow the relation $K = \frac{1}{at}\left(\frac{1}{C} - \frac{1}{C^0}\right)$, where a is the degree of dissociation of the hydrochloric acid. The order of the relative reactivities is the same for each temperature; this order is formamide, propionamide, acetamide, *iso*butyramide, capronamide, butyramide, valeramide. The temperature coefficients of reactivity are very large, and the velocity constants closely follow the temperature law,

$$\log K = \log K_0 + B\left(\frac{1}{T} - \frac{1}{T}\right).$$

A relation between the reactivity of the amides at constant temperature and the strength of the corresponding organic acids was indicated. The relative reactivities of the amides were also evaluated at "corresponding" temperatures and these values were shown to be nearly independent of temperature.

45. "The rusting of iron." By Wyndham Rowland Dunstan.

As a result of a long series of experiments (Dunstan, Jowett, and Goulding, *Trans.*, 1905, **87**, 1548), it was shown that the rusting of iron can take place in the absence of carbonic acid, and that only iron, oxygen, and liquid water are necessary for rusting to occur. In order to elucidate the chemical change involved, and to explain the inhibiting effect on the rusting of iron produced by some substances and especially by alkalis and potassium dichromate, the working hypothesis was suggested that the formation of hydrogen peroxide is concerned in the change, rusting being prevented by those substances which are capable of decomposing the peroxide.

Recently, Dr. Gerald T. Moody (*Trans.*, 1906, **89**, 720) has published an account of experiments he has made which in his opinion prove that iron cannot rust in the absence of carbon dioxide. In the experiments recorded by the present author (*loc. cit.*) elaborate precautions were taken to ensure the absence of carbon dioxide, but it has been thought desirable to repeat the experiments made under somewhat different conditions by Dr. Moody. His conclusions have not, however, been confirmed; the results of experiments carried out in the manner described by him show that iron rusts freely in the absence of carbonic acid provided that iron, oxygen, and liquid water are brought together.

46. "Contributions to the chemistry of the rare earths. Part II." By Mario Esposito.

The methods of Muthmann and Böhm and Pattinson and Clarke for the preparation of ceria have been found to give a fairly pure product. Oxidation with potassium permanganate, according to Drossbach and Böhm's method, is probably the most rapid and satisfactory way of obtaining almost pure ceria.

Lanthana and old didymia can be separated by fractional crystallisation of the oxalates from strong nitric acid, but the process is not advantageous. Lanthana is best obtained by a modification of the method of Auer von Welsbach (fractional crystallisation of the double ammonium nitrates), which at the same time effects the separation of neodymia and praseodymia, the chief constituents of old didymia. After one hundred and ten fractionations, lanthana, praseodymia, and neodymia were obtained in a state of considerable purity.

47. "Derivatives of multivalent iodine. Part III. Action of heat on iodobenzene dichloride, and on the *m*- and *p*-nitro- and *p*-chloro-derivatives." By William Caldwell and Emil Alphonse Werner.

The authors have found that when iodobenzene dichloride is heated it undergoes sudden decomposition at 112—136° according to the rate of heating, the main change resulting in the formation of *p*-chloroiodobenzene. Only from 17 to 27 per cent. of the theoretical amount of chlorine is evolved in the free state. Rapid heating favours the formation of the substitution derivative. Whilst *o*- and *p*-iodonitrobenzene dichloride, when heated, decompose quantitatively in accordance with the equation,

$$C_6H_4(NO_2)\cdot ICl_2 = C_6H_4(NO_2)I + Cl_2,$$

the *m*-derivative loses from 72—73 per cent. of its chlorine in the free state, a substitution derivative being produced in corresponding proportion.

p-Chloroiodobenzene forms a dichloride, $C_6H_4Cl{\cdot}ICl_2$, which decomposes at 112°, the proportion of chlorine evolved in the free state amounting to 72 per cent. of the theoretical for the loss of two atoms. Thus the nitro-group in the ortho- and para-positions completely prevents the formation of substitution products, whilst chlorine in the para- has the same inhibiting effect as the nitro-group in the meta-position.

48. "The organic phosphorus compound formed by yeast-juice from soluble phosphates. Preliminary notice." By William John Young.

It has been shown by Harden and Young (*Proc.*, 1905, **21**, 189; *Proc. Roy. Soc.*, 1906, **77**, *B.*, 405) that when soluble phosphates are added to a fermenting mixture of yeast-juice and glucose a large increase in the rate of evolution of carbon dioxide is observed. This rate soon diminishes until a constant rate is attained, which is usually approximately equal to that of the original yeast-juice and glucose. It has been further shown that at the end of this period of increased fermentation, the phosphate has undergone some alteration, and is no longer present in a form precipitable by magnesium citrate mixture, and it was suggested that a combination with the glucose to form a phosphoric acid ester had taken place.

Experiments on the chemical nature of this compound have been carried out, and although not yet complete, it has been thought advisable to communicate a preliminary notice of the results so far obtained, in view of the publication of Iwanoff (*Zeit. physiol. Chem.*, 1907, **50**, 281), who appears to have obtained the same substance independently.

A lead salt of the compound was prepared from the fermentation mixture by first removing any free phosphate by magnesium nitrate and then adding lead nitrate. Analyses of two preparations, in which the carbon, hydrogen, lead, and phosphorus were determined, gave the empirical formula $C_3H_5O_6PPb$.

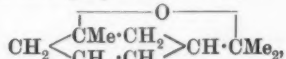
On suspending this salt in water and removing the lead with hydrogen sulphide, an acid solution is obtained which reduces Fehling's solution and gives Mohlisch's α-naphthol reaction. It is slightly dextrorotatory, and can be titrated with alkalis, using phenolphthalein as indicator, in a similar manner to phosphoric acid. On evaporating to dryness on the water-bath a charred mass is left which contains free phosphoric acid and has a strong odour of caramel, whilst on evapora-

tion at the ordinary temperature in a vacuum over sulphuric acid a syrupy mass is left, which soon darkens in colour and decomposes.

When the solution is boiled for several hours the compound is slowly hydrolysed, phosphoric acid being set free, and a substance formed which reduces Fehling's solution more strongly than the acid itself, and rotates the plane of polarised light to the left. The nature of this reducing substance has not been exactly determined and experiments with this object are in progress.

49. "Experiments on the synthesis of the terpenes. Part X. Synthesis of carvestrene and its derivatives." By William Henry Perkin, jun., and George Tattersall.

Continuing their work on the synthesis of carvestrene (*Proc.*, 1906, **22**, 268), the authors have prepared m-*cineol*,



by the action of magnesium methyl iodide on ethyl *cyclo*hexanone-3-carboxylic acid, and the *cis*- and *trans*-modifications of m-*menthane*-1 : 8-*diol*, , have also been obtained.

ADDITIONS TO THE LIBRARY.

II. *By Purchase.*

Arrhenius, *Svante.* Immunochemie. Anwendungen der physikalischen Chemie auf die Lehre von den physiologischen Antikörpern. Uebersetzt von *Alexis* **Finkelstein**. pp. vii + 204. Leipzig 1907. (*Recd.* 20/2/07.)

Berthelot, *Marcellin.* Traité pratique l'analyse des gaz. pp. ix + 483. ill. Paris 1906. (*Recd.* 20/2/07.)

Calmette, *A.* Avec la collaboration de *E.* **Rolants**, *F.* **Constant**, *E.* **Boullanger**, *L.* **Massol**, et *A.* **Buisine.** Recherches sur l'épuration biologique et chimique des eaux d'égout. 2 vols. pp. v + 194, iv + 314. ill. Paris 1905—7. (*Recd.* 20/2/07.)

Donath, *Eduard*, und **Frenzel**, *Karl.* Die technische Ausnutzung des atmospärischen Stickstoffes. pp. v + 250. Leipzig 1907. (*Recd.* 20/2/07.)

Wiley, *Harvey W.* Principles and practice of agricultural analysis. A manual for the study of soils, fertilizers, and agricultural products. Second edition. Vol. I, Soils. pp. xii + 636. Easton, Pa. 1906. (*Recd.* 20/2/07.)

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Métropole, at 6.30 for 7 o'clock, on **Friday, March 22nd, 1907** (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Friday, March 15th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the Annual General Meeting on Friday, March 22nd, the President will deliver an address entitled "The Position and Prospects of Chemical Research in Great Britain."

On Thursday, June 13th, Professor J. B. Farmer, F.R.S., will discourse on "Some Borderline Problems in Botany."

ERRATA.

1906. P. 197, line 6 from bottom, and p. 198, line 6 from top, *for* "acetophenyloxalic" *read* "benzoylpyruvic."

1907. P. 33, line 15 from top, *for* "3-dimethylphenonaphthoxazone" *read* "3-dimethylaminophenonaphthoxazone."

At the next Ordinary Meeting, on **Thursday**, March **7th**, 1907, the following papers will be communicated:

"The constitution of chaulmoogric and hydnocarpic acids." By M. Barrowcliff and F. B. Power.

"Volume changes which accompany transformations in the system $Na_2S_2O_3,5H_2O$." By H. M. Dawson and C. G. Jackson.

"Hydrolysis of amygdalin by acids." By R. J. Caldwell and S. L. Courtauld.

"Mandelonitrile-glucosides. The constitution of prulaurasin." By R. J. Caldwell and S. L. Courtauld.

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Issued 15/3/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 322.

Thursday, March 7th, 1907, at 8.30 p.m., Professor R. MELDOLA, F.R.S., President, in the Chair.

Messrs. Frank Baker, F. S. Benton, L. H. Berry, F. J. Harris, A. T. King, B. D. Porritt, F. G. P. Remfry, A. H. Salway, and Frank Tutin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. :

John Arthur Cunningham, B.A., Presidency College, Calcutta, India.

Samuel Duckworth, M.Sc., 78, Alexandra Road, Lowestoft, Suffolk.

Arthur George Harrington, Rochford, Westbury Road, Ealing, W.

Frederic William Rixon, M.Sc., Ph.D., Powderham Road, Newton Abbot, Devonshire.

William Griffiths Tonner, B.Sc., 26, Gordon Road, Kingston-on-Thames.

The CHAIRMAN read the names of the Fellows recommended by the Council for election as official and ordinary Members of Council, and announced that the name of Mr. F. H. Streatfeild had been proposed by another Fellow as an ordinary Member of Council.

Of the following papers, those marked * were read:

***50. "The constitution of chaulmoogric and hydnocarpic acids." By Marmaduke Barrowcliff and Frederick Belding Power.**

In previous communications (Power and Gornall, *Trans.*, 1904, **85**, 838, 851) the isolation and properties of chaulmoogric acid, $C_{18}H_{32}O_2$ (m. p. 68°), were described. It is optically active, having $[\alpha]_D^1$ +56°, and was shown to contain both a closed ring and an ethylenic linking.

When chaulmoogric acid is oxidised in alkaline solution with limited quantities of potassium permanganate it yields *α-dihydroxydihydrochaulmoogric acid*, $C_{18}N_{32}O_2(OH)_2$ (m. p. 105°; $[\alpha]_D$ +11·6°), *β-dihydroxydihydrochaulmoogric acid*, $C_{18}H_{32}O_2(OH)_2$ (m. p. 93°; $[\alpha]_D$ −14·2°), and *hydroxyketodihydrochaulmoogric acid*, $C_{18}H_{32}O_4$. Further oxidation gives, on the one hand, an optically inactive tricarboxylic acid, $C_{18}H_{32}O_6$ (m. p. 68°), which is n-*pentadecane-aa'γ-tricarboxylic acid*, $CO_2H\cdot[CH_2]_2\cdot CH(CO_2H)\cdot[CH_2]_{12}\cdot CO_2H$, and, on the other hand, formic acid and a keto-acid, $C_{17}H_{30}O_5$, previously described (*loc. cit.*), which is now shown to possess the formula

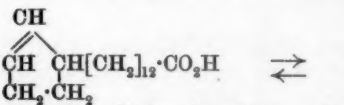
$$CO_2H\cdot[CH_2]_2\cdot CO\cdot[CH_2]_{12}\cdot CO_2H.$$

The latter compound, on oxidation, yields *n*-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, and *n*-undecanedicarboxylic acid,

$$[CH_2]_{11}(CO_2H)_2.$$

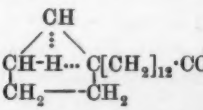
By the addition of hydrogen bromide to chaulmoogric acid, and its subsequent elimination, an optically active mixture of acids is obtained, which, when oxidised, furnishes a keto-acid, $C_{18}H_{32}O_5$ (m. p. 126°), to which the formula, $CO_2H\cdot CH_2\cdot CHMe\cdot CO\cdot[CH_2]_{12}\cdot CO_2H$, is ascribed.

The results obtained can be explained by assigning to chaulmoogric acid both the following formulæ, and considering it to exist in a state of tautomerism between the two structures.

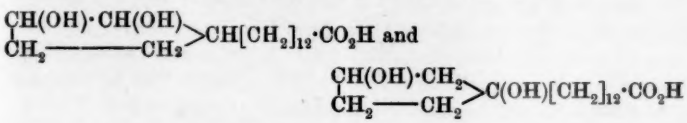


1-α-*Carboxy*-n-*dodecyl*-Δ⁴-cyclo*pentene*. 1-α-*Carboxy*-n-*dodecyl*-1 : 4-bicyclo*pentane*.

Its constitution may therefore be represented by the following formula:

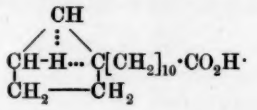


To the dihydroxydihydrochaulmoogric acids the formulæ :



are ascribed, whilst dihydrochaulmoogric acid, $C_{18}H_{34}O_2$, is considered to be a mixture of *α-carboxy*-n-*dodecyl*cyclo*pentane* and i-*α-carboxy*-n-*dodecyl*-2-*methyl*cyclo*butane*.

Hydnocarpic acid, $C_{16}H_{28}O_2$ (m. p. 60° ; $[\alpha]_D$ +68°), a homologue of chaulmoogric acid (*Trans.*, 1905, **87**, 884), yielded on oxidation an acid, $C_{16}H_{28}O_6$ (m. p. 60°), which is n-*tridecane-aa'γ-tricarboxylic acid*, $CO_2H{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}[CH_2]_{10}{\cdot}CO_2H$, together with *n*-decanedicarboxylic acid, $[CH_2]_{10}(CO_2H)_2$. Its constitution may accordingly be represented by the following formula :



***51. "Hydrolysis of amygdalin by acids." By Robert John Caldwell and Stephen Lewis Courtauld.**

With the object of obtaining further evidence as to the constitution of amygdalin, the authors have systematically studied the action of acids in comparison with that of enzymes on this "bioside."

The results show that, although amygdalin is ultimately resolved by acids into hydrogen cyanide, benzaldehyde, and two molecular proportions of glucose, the separation of the glucose is effected in two stages. The hydrolysis of the biose section of the molecule proceeds only at about one-sixth of the rate at which maltose is hydrolysed under like conditions. By carefully hydrolysing amygdalin by means of a normal solution of hydrogen chloride at 60°, the authors have prepared the mandelonitrile glucoside which E. Fischer obtained by subjecting the bioside to the action of an extract of yeast ; this method of obtaining the glucoside appears to be in some respects advantageous, the product being more easily purified.

***52. "Mandelonitrile glucosides. Prulaurasin." By Robert John Caldwell and Stephen Lewis Courtauld.**

In order to ascertain whether the glucoside prepared by hydrolysing amygdalin is a direct product or one which has undergone isomeric

change, the authors have subjected it to the action of alkalis; they find that it is converted into a substance identical with the isomeric substance prulaurasin, isolated by Hérissey from laurel leaves. Fischer's glucoside therefore bears the same relation to prulaurasin as amygdalin bears to the *iso*amygdalin described by Dakin, which is to be regarded as the derivative of inactive mandelonitrile, amygdalin and Fischer's glucoside being derived from *l*-mandelonitrile. As the rotatory power of prulaurasin is intermediate between that of Fischer's glucoside and that of sambunigrin, the second isomeride of Fischer's glucoside recently described by Bourquelot and Danjou, the latter must be regarded as the β-glucoside of *d*-mandelonitrile.

Characteristic acetyl derivatives have been prepared from amygdalin, *iso*amygdalin, Fischer's glucoside, and prulaurasin.

*53. "The hydrolysis of amygdalin by emulsin." By Samuel James Manson Auld.

Although amygdalin is generally described as the maltoside of benzaldehydecyanohydrin since on hydrolysis it produces two molecules of dextrose, it is probable that the biose residue is an unknown $\alpha\beta$-disaccharide capable of hydrolysis both by emulsin and maltase.

The hydrolysis of amygdalin by emulsin may proceed in three ways, depending on the mode of attachment of the emulsin. Either mandelonitrile glucoside and dextrose are first produced with subsequent hydrolysis of the former, or benzaldehydecyanohydrin and the $\alpha\beta$-disaccharide are formed, and the latter then resolves into two molecules of dextrose, or, lastly, the amygdalin may undergo fission into the three components by direct abstraction of the dextrose residue attached to the benzaldehydecyanohydrin molecule. The experiments so far carried out indicate that the second process of cleavage is the true one.

Discussion (on the three foregoing papers).

Dr. McKenzie asked whether two mandelonitrile glucosides had been obtained, where the relationship is similar to that which exists between amygdalin and *iso*amygdalin, and, further, if the mandelonitrile glucoside described was racemic as regards the mandelic complex, had the fractional hydrolysis of this compound been studied?

Dr. Henry stated that the report on "Cyanogenesis in Plants," prepared by Professor Dunstan and himself for the York Meeting of the British Association, was mainly a compilation of the published information then available on the subject, and consequently the reference there to amygdalin as a derivative of maltose did not commit the

authors of the Report to that view of the constitution of the biose residue of the glucoside, and, in fact, the nature of the sugar residue of amygdalin was then under investigation by Dr. Auld, who had been associated recently with the authors in their work on cyanogenetic glucosides.

The interest shown of late in this subject had been created by the work done at the Imperial Institute since 1900, and it had been the intention of Professor Dunstan and himself to investigate fully the relationship of Fischer's mandelonitrile glucoside to prulaurasin and sambunigrin. In view of the fact that Professor Dunstan and he were well known to be at work in this field, it was unfortunate that Messrs. Caldwell and Courtauld had, without consultation, commenced work on these three isomerides.

Dr. AULD regretted that he was not aware that this investigation had been undertaken, as he had been at work on the problem of the constitution of the biose residue of amygdalin for some time. It was an entirely erroneous assumption that the maltose structure of this residue had been taken for granted. Dr. Henry's article in *Science Progress* (July, 1906) clearly showed that the exact nature of the sugar residue in these glucosides had not been settled. The results of Messrs. Caldwell and Courtauld's communication did not throw much new light on the actual configuration of the biose residue.

***54. "Electrolytic reduction. Part III." By Herbert Drake Law.**

The products of electrolytic reduction of the aromatic aldehydes in alkaline solution are compounds of the hydrobenzoin type, but this reaction is completely altered when a methyl group is substituted in the ortho- or meta-position of the benzene nucleus. In the latter case, compounds of a resinous nature are obtained. Thus *p*-tolualdehyde gives a well-defined crystalline substance, whilst *m*- and *o*-tolualdehydes yield nothing but resins. The resinifying effect of a single substitution may, however, be neutralised by the introduction of a second group in a similar position on the opposite side of the nucleus. Thus with 3 : 5-dimethylbenzaldehyde a crystalline product is obtained, whilst 2 : 4-dimethylbenzaldehyde yields 40 per cent. of resin. Similar results were given by other aldehydes.

In acid solution, the products differed greatly at different temperatures. Thus in cold solutions primary alcohols were obtained to a large extent, but at 40° the product was of the hydrobenzoin type. Stilbenes and saturated hydrocarbons were also obtained.

Discussion.

The President asked whether, in writing the formulæ of the aromatic aldehydes sometimes with the Kekulé benzene ring and at others with the "centric" arrangement of bonds, the author intended to convey the idea that the Kekulé formula represented the benzene molecule as unsaturated, and the "centric" formula as saturated.

Mr. Law, in reply, said that the concentric formula best represents the constitution of the benzene nucleus. The introduction of a strain across the molecule distorts this configuration, the greatest mechanical effect being produced for a substitution in the ortho-position. In the latter case, Kekulé's formula probably nearly represents the state of the molecule. Between these two extremes it is possible that many other forms may exist.

*55. "New cerium salts."

By Gilbert Thomas Morgan and Edward Cohen.

Although in many cases the cerous salts of carboxylic acids, such as the cinnamate, are insoluble, uncrystallisable substances, it has now been shown that the aromatic sulphonates of this element are usually soluble, crystalline compounds resembling the thorium sulphonates previously described by one of the authors (*Abstr.*, 1904, i, 892). A representative series of these cerous sulphonates has been prepared together with several other salts of inorganic and organic acids.

Discussion.

Dr. Power called attention to the formula of cerium oxalate, which Dr. Morgan had referred to as being $Ce_2(C_2O_4)_3,9H_2O$, and stated that an investigation of this salt, conducted some years ago by Mr. Frank Shedden and himself (*J. Soc. Chem. Ind.*, 1900, 19, 636), had conclusively shown that it contains 10 molecules of water. It was thus perfectly analogous in composition to the oxalates of lanthanum and didymium, which may be represented by the general formula

$$R'''_2(C_2O_4)_3,10H_2O.$$

Dr. Morgan stated that he had, quite incidentally, represented cerous oxalate as $Ce_2(C_2O_4)_3,9H_2O$, as this appeared to be the accepted formula for this well-known salt, and was thus given in current works on pharmacy. He had not noticed Dr. Power's correction which showed that the oxalate was in reality a decahydrate, $Ce_2(C_2O_4)_3,10H_2O$.

56. "Volume changes which accompany transformations in the system $Na_2S_2O_3 : 5H_2O$." By Harry Medforth Dawson and Colin Gyrth Jackson.

The changes which take place in the system $Na_2S_2O_3 : 5H_2O$ when subjected to certain temperature variations have been investigated by the dilatometric method. Volume temperature curves which indicate the relationship of the various forms of the system were described. At a temperature of 25° the system has been obtained in the following six forms, each characterised by a definite volume: (1) primary pentahydrate, (2) secondary pentahydrate, (3) secondary tetrahydrate and saturated solution, (4) primary pentahydrate and saturated solution, (5) secondary monohydrate and saturated solution, (6) liquid.

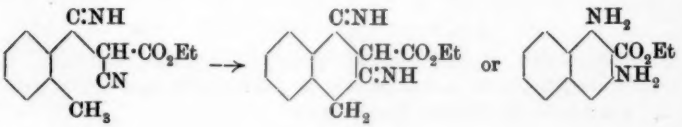
With an accurately calibrated dilatometer the volume occupied by the supercooled liquid of the composition $Na_2S_2O_3 : 5H_2O$ can be directly compared with the volumes of the primary and secondary pentahydrates and the specific gravities of these obtained with considerable accuracy. The transformation of the metastable secondary pentahydrate into the stable primary form affords an interesting lecture experiment.

57. "Depression of the freezing point of aqueous solutions of hydrogen peroxide by potassium persulphate and other compounds." By Thomas Slater Price.

Potassium persulphate causes a less molecular depression of the freezing point of aqueous solutions of hydrogen peroxide than it does of water, and the conclusion is drawn that an unstable compound is formed in solution (compare Friend, *Trans.*, 1906, **89**, 1092); similar results hold for potassium sulphate and hydrogen peroxide. In the case of sulphuric acid the molecular depression of hydrogen peroxide solutions is greater than that of water; this confirms the results of Jones and Murray (*Amer. Chem. J.*, 1903, **30**, 205), that sulphuric acid is dissociated to a greater extent in aqueous hydrogen peroxide than in water. Potassium hydrogen sulphate and hydrogen peroxide interact in concentrated solution with the production of potassium permonosulphate—no potassium persulphate ($K_2S_2O_8$) is formed—but it was not possible to obtain the pure salt. It was pointed out that a solution of potassium permonosulphate, in the presence of free acid, is much more stable than has been hitherto supposed.

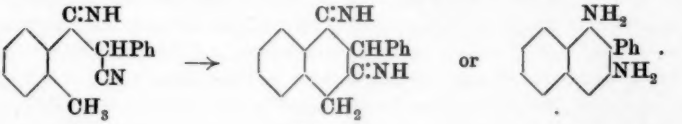
58. "The formation and reactions of imino-compounds. Part III. The formation of 1 : 3-naphthylenediamine and its derivatives from *o*-toluonitrile." By Ernest Francis Joseph Atkinson, Harry Ingham, and Jocelyn Field Thorpe.

In Part II of this series it was shown that derivatives of benzene containing a saturated side chain of three carbon atoms substituted in the α-position by the nitrile group and in the β-position by the imino-group pass on treatment with cold concentrated sulphuric acid into derivatives of 1 : 3-naphthylenediamine. The authors have now applied this reaction to those derivatives of benzene which possess a saturated side chain of two carbon atoms substituted in the α-position by a nitrile group and in the β-position by an imino-group, and which contain a methyl group in the benzene ring in the ortho-position in respect to the side chain. The two compounds chosen to illustrate this generalisation were ethyl β-imino-α-cyano-β-*o*-tolylpropionate (I), which was found to be quantitatively converted into ethyl 1 : 3-naphthylenediamine-2-carboxylate (II) on being dissolved in cold concentrated sulphuric acid :



(I) (II)

and β-imino-α-cyano-α-phenyl-β-*o*-tolylethane (III), which under the same conditions passed into 1 : 3-diamino-2-phenylnaphthalene (IV) :

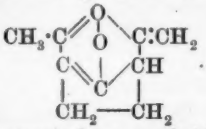


(III) (IV)

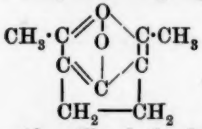
Evidence was also brought forward indicating that the closing of the ring both in the present instances and also in those dealt with in Part II is due to the formation of a definite addition product formed by the action of concentrated sulphuric acid on the nitrile group.

59. "The action of ethylene dibromide and of propylene dibromide on the disodium derivative of diacetylacetone."
By Alexander William Bain.

By the action of ethylene dibromide on anhydrous disodium diacetylacetone, the author has isolated a *compound* having the formula $C_9H_{10}O_2$, to which he ascribes the constitution

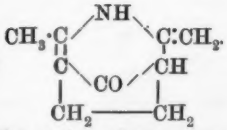


This substance melts at 62—63°, and possesses the remarkable faculty of undergoing isomeric change to a pyrone derivative, namely,



, when heated with concentrated hydrochloric acid. The *hydrochloride* and *platinichloride* of this derivative have been prepared and analysed.

Ammonia reacts with the compound to give



Similar derivatives have been prepared by the action of propylene dibromide, but both alkyl and alkylene halides of higher molecular weight react with great difficulty and then only to give very unstable compounds.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Archbutt, *Leonard,* and **Deeley,** *R. Mountford.* Lubrication and lubricants. A treatise on the theory and practice of lubrication, and on the nature, properties, and testing of lubricants. 2nd edition. pp. xxxi + 528. ill. London 1907. (*Recd.* 6/3/07.)

From L. Archbutt, Esq.

Bernthsen, *A.* A text-book of organic chemistry. The English translation from the German, edited and revised to date by *J. J.* **Sudborough.** pp. xvi + 658. London 1906. (*Recd.* 6/3/07.)

From Professor J. J. Sudborough.

Freeman, *John R.* On the safeguarding of life in theatres. An Address made at the opening of the Annual Meeting of the American Society of Mechanical Engineers in New York City, December 4, 1905. Reprinted from the Transactions of the Society. pp. 106. ill. [New York] 1906. (*Recd.* 1/3/07.) From the Author.

Pauli, *Wolfgang.* Physical chemistry in the service of medicine. Authorised translation by *Martin H.* **Fischer.** pp. ix + 156. New York 1907. (*Recd.* 27/2/07.)

From the Publishers: Messrs. John Wiley and Sons.

Plimmer, *R. H. Aders.* Practical physiological chemistry. 2 vols. pp. 55, 83. London [1907]. (*Recd.* 5/3/07.) From the Author.

Pozzi-Escot, *Em.* The toxins and venoms, and their antibodies. Authorised translation by *Alfred I.* **Cohn.** pp. vii + 101. New York 1906. (*Recd.* 27/2/07.)

From the Publishers: Messrs. John Wiley and Sons.

Shepperson, *William.* Field to dairy. 2nd edition. pp. 65. London 1907. (*Recd.* 28/2/07.) From the Author.

West Indies, *Imperial Department of Agriculture.* Lectures to sugar planters. pp. viii + 176. [Barbados] 1906. (*Recd.* 23/2/07.)

From the Department.

II. *By Purchase.*

Hammarsten, *Olof.* Festschrift Olof Hammersten zu seinem fünfundsechzigsten Geburtstage den 21 sten August 1906, gewidmet. pp. xxxi + [635]. Upsala 1906. (*Recd.* 23/2/07.)

Ries, *Heinrich.* Clays: their occurrence, properties, and uses. With especial reference to those of the United States. pp. xvi + 490. ill. New York 1906. (*Recd.* 23/2/07.)

Thomson, *J. J.* Conduction of electricity through gases. 2nd edition. pp. viii + 678. ill. Cambridge 1906. (*Recd.* 23/2/07.)

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Whitehall Rooms, Hotel Métropole, at 6.30 for 7 o'clock, on **Friday, March 22nd, 1907** (the day fixed for the Annual General Meeting).

The price of the tickets will be One Guinea each, including wine.

All applications for tickets must be received not later than Friday, March 15th next.

Tickets will be forwarded to Fellows on receipt of a remittance for the number required, made payable to "Mr. S. E. Carr" and addressed to the Assistant Secretary, Chemical Society, Burlington House, W.

At the Annual General Meeting on Friday, March 22nd, the President will deliver an address entitled "The Position and Prospects of Chemical Research in Great Britain."

At the next Ordinary Meeting on **Thursday, March 21, 1907,** the following papers will be communicated:

"The synthesis of polypeptides." By Emil Fischer.

"Organic derivatives of silicon. Part III. *dl*-Benzylmethylethylpropylsilicane and experiments on the resolution of its sulphonic derivative." By F. S. Kipping.

"The reduction of carbon dioxide to formaldehyde in aqueous solutions." By H. J. H. Fenton.

"The mechanism of the rusting of iron." By G. T. Moody.

"Some compounds of guanidine with sugars. Part I." By R. S. Morrell and A. E. Bellars.

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Issued 28/3/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 323.

Thursday, March 21st, 1907, at 8.30 p.m., Sir HENRY E. ROSCOE, F.R.S., Past President, in the Chair.

Messrs. W. J. Bowis, L. M. Deane, E. W. L. Foxall, W. Godden, C. M. W. Grieb, and J. L. Simonsen were formally admitted Fellows of the Society.

Before commencing the business of the Society, Sir HENRY ROSCOE said that the Fellows would have learnt with great regret of the loss which their science, and especially French chemistry, had to deplore in the sudden and pathetic death of Marcellin Berthelot. This was not the occasion to dwell upon the important work which he had accomplished or on his noble character. These considerations would doubtless be fully dealt with hereafter. All that the Fellows of the Society now could do was to express their grief at his death and their sympathy with his family.

The CHAIRMAN also alluded with feeling to the death of their old Fellow, Prof. Warington.

Certificates were read for the first time in favour of Messrs.:

Kenneth Somerville Caldwell, B.Sc., Ph.D., St. Bartholomew's Hospital, E.C.

John Jacob Fox, 6, Alkham Road, Stamford Hill, N.

Joseph Henry Hall, B.Sc., 84, The Grove, Wandsworth, S.W.
Thomas Featherstone Harvey, 84, Henry Road, West Bridgford, Nottingham.
Edward Houghton, Glenhyrst, 106, Saltergate, Chesterfield.
Carl Lewis, P.O. Box 36, Johannesburg, S. Africa.
Herbert Victor Mitchell, 26, Brookfield Avenue, Walthamstow.
George Colleymore Sturrock, Capt., R.A., Arubankad, Nilgiris, India.
Sam Mortimer Sutcliffe, 4, Clive Place, Bradford.

Of the following papers, those marked * were read:

*60. "Synthesis of polypeptides." By Emil Fischer.

Continuing his work on the synthesis of polypeptides the author has prepared an octadecapeptide containing fifteen glycocoll and three *l*-leucine residues.

Pentaglycylglycine was allowed to react with *d*-bromo*iso*capronyldiglycylglycyl chloride, and the product so obtained was treated with ammonia with formation of *l*-leucyloctaglycylglycine. By a repetition of this series of reactions the octadecapeptide, *l*-leucyltriglycyl-*l*-leucyltriglycyl-*l*-leucyloctaglycylglycine,

$$NH_2\cdot CH(C_4H_9)\cdot CO[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(C_4H_9)\cdot CO[NH\cdot CH_2\cdot CO]_3-$$
$$-NH\cdot CH(C_4H_9)\cdot CO[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H,$$

has been synthesised.

Discussion.

The Chairman said that he only voiced the feeling of the Society when he expressed his admiration for the interesting and remarkable lecture to which they had all listened with pleasure. In reciprocating to the full the words which had fallen from Professor Armstrong's lips as to the wonderful character of the researches which Professor Fischer had described, he remarked that whilst they looked upon these researches as typical of the great strides made in German chemical science, he ventured to think that Professor Fischer would agree with him when he said that he believed that the work done by the Fellows of our Chemical Society at the present time would bear not unfavourable comparison, both as to quality and quantity, with that which is now being carried out in Germany. Indeed, when he looked back to the early years of the Society, as his friend Sir William Perkin and he could do, and remembered the progress which it had made, the activity which the Fellows of the Society had shown in recent years in advancing the progress of their science struck him as most remarkable, and this in spite of the many drawbacks which have often been said

to discourage original research in England. We could not indeed vie with Germany in the special department of research which had just been laid before the Society, and this for a very simple reason, that there was only one Emil Fischer.

***61. "Organic derivatives of silicon. Part III. *dl*-Benzylmethylethylpropylsilicane and experiments on the resolution of its sulphonic derivative." By Frederic Stanley Kipping.**

dl-Benzylmethylethylpropylsilicane, SiMeEtPrBz (*Proc.*, 1905, **21**, 65), is sulphonated by sulphuric acid at about 130°, yielding a mixture of acids of which two were isolated in the form of their *l*-menthylamine salts.

Analyses of one of these salts seem to show that it is derived from *benzylethylpropylsilicolsulphonic acid* and has the formula

$$EtPrSi(OH)\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N,$$

but as it is formed in small amount only it has not been very thoroughly investigated; the formation of such an acid from the silicohydrocarbon would necessitate the hydrolytic separation of the methyl group in a manner similar to that in which the phenyl group is displaced on sulphonating phenylbenzylethylpropylsilicane (*Trans.*, 1907, **91**, 224). The salt crystallises in prisms and melts at 210—212°.

The second *l*-menthylamine salt isolated from the mixture is derived from di-*benzylmethylethylpropylsilicanesulphonic acid* and has the formula $SiMeEtPr\cdot CH_2\cdot C_6H_4\cdot SO_3H,C_{10}H_{21}N$. This compound is much more easily obtained from the product of the sulphonation of benzylmethylethylpropylsilicane with chlorosulphonic acid. It crystallises best ($+2H_2O$) from wet, light petroleum and when dehydrated melts at 122—123°.

The *l*-*menthylamine*, *quinine*, *cinchonidine*, *cinchonine*, *narcotine* and several other salts of this *dl*-silicanesulphonic acid have been crystallised fractionally under various conditions, but without the faintest indication of a resolution of the acid having been observed.

***62. "The reduction of carbon dioxide to formaldehyde in aqueous solution." Henry John Horstman Fenton.**

The author finds that by the action of metallic magnesium, under appropriate conditions, on an aqueous solution of carbon dioxide, recognisable quantities of formaldehyde can be obtained and that the amounts are considerably increased if weak bases, such as ammonia, aniline, phenylhydrazine or aluminium hydroxide, are also present.

Further, it is found that formic acid may readily be reduced, in part at any rate, to formaldehyde by the action of magnesium so that the desired reduction of carbon dioxide may be effected also in two stages, with formic acid as the intermediate product.

*63. "The mechanism of the rusting of iron." By Gerald Tattersall Moody.

The author has previously shown that the presence of acid is essential for rusting to occur. The following experiment enables the exact mechanism of the production of rust to be visualised :—In the bottom of a glass cylinder are placed some rods of bright iron such as French nails. These are only loosely packed, for the most part heads upward, and are so arranged that some of them remain vertical whilst others occupy inclined positions. Recently boiled distilled water is then poured into the cylinder until it stands about one and a half inches above the heads of the nails. The mouth of the cylinder is loosely closed with a sheet of paper so as to exclude dust and at the same time to allow free access of air to the water, whereby carbonic acid and oxygen are absorbed. In the course of twenty-four hours the water shows signs of becoming turbid and shortly afterwards a copious separation of brown particles from the solution is distinctly observed. These brown particles are continuously formed and gradually settle on the heads of the nails and on the upper parts only of those nails which are inclined. The under parts of the inclined nails and the vertical nails remain bright, no general corrosion of the surfaces being observable. At the end of seven days a thick layer of hydrated ferric oxide has collected on the upper surfaces of the nails and also on the bottom of the cylinder. If a sheet of hardened filter paper or some other material, which allows of diffusion, be placed in a horizontal position immediately over the nails at the beginning of the experiment, the rust which separates from the solution above it gradually collects on its upper surface and eventually forms a thick layer.

The separation of the rust from the water and its non-formation on the surface of the iron can be explained only as an oxidation of ferrous iron actually in solution. This is in strict accordance with the experimental evidence already advanced and shows that, in rusting, iron is first dissolved with formation of ferrous salt which subsequently oxidises to rust.

Discussion.

The Chairman remarked that all those present must be much struck by the extremely simple and convincing experiments which the author had described, showing that the first step towards the rusting

of iron was that the metal entered into solution in the liquid. He ventured to doubt, however, whether the author had even now got to the bottom of the subject, simple though it apparently was, because he had not explained how the solution of the metal was effected, whether this solution occurred in presence of carbonic acid only or whether in its absence.

Dr. MOODY said that he had already described experiments which showed conclusively that the presence of acid is essential for rusting to occur (*Trans.*, 1906, **89**, 720). In absence of acid, pure iron was allowed to remain in contact with water and oxygen for several weeks without even one speck of rust being formed, and without the iron undergoing any change either in appearance or in weight. It was specially noteworthy that when pure iron was placed in a dilute solution of hydrogen peroxide free from acid, no oxidation or other change in the iron occurred, although oxygen was freely evolved from every part of the immersed metal. In this way the indifference of iron towards oxygen in presence of water could be easily and conclusively demonstrated. In the experiment he had shown the Society that evening, the iron was undoubtedly dissolved by carbonic acid, and the ferrous bicarbonate thus formed was converted into rust by oxygen, which, simultaneously with the carbonic acid, diffused into the solution from the atmosphere.

***64. "Influence of non-electrolytes and electrolytes on the solubility of sparingly soluble gases in water. The question of hydrates in solution." By James Charles Philip.**

It is suggested that the influence of non-electrolytes and electrolytes on the solubility of gases may be adequately interpreted by reference to two factors. Firstly, it may be supposed that the non-electrolyte or electrolyte takes no part in the absorption, and accordingly the standard absorbing volume should be not 1 c.c. or 1 litre of the solution, but that volume of the solution which contains 1 gram or 1000 grams of the pure solvent. Secondly, hydration of the non-electrolyte or electrolyte may occur, and it may be supposed that the solvent which is thus attached is no longer free to absorb the gas. These suggestions have been tested with satisfactory results by reference to available experimental data, and the values found for the average molecular hydration of dissolved salts are in fair agreement with the values reached by other and widely different methods.

Discussion.

Sir William Ramsay asked whether it must not be held that both the solvent and the solute take part in dissolving a gas. For example, a solution of sugar in water is a mixture of liquid sugar and liquid water, and it might be supposed that hydrogen would dissolve in both water and in sugar according to its solubility in each, and to their relative amount.

Mr. R. J. Caldwell drew attention to the fact that Euler and others had recognised that the absorption coefficients of the permanent gases, as well as the solubility of ethyl acetate, are equally affected by the presence of dissolved solids. It had long been clear to him that this regularity could be accounted for by assuming that a diminution of the amount of free water was caused by the formation of hydrates of the dissolved substance; most of the material had been collected for a communication on the subject. From the very accurate values given by Winkler for the solubility of oxygen, making due allowance for the fact that Winkler used volume-normal solutions, he had calculated that the average degree of hydration of calcium chloride in a solution of gram-molecular strength (weight-normal) was in the ratio

$$CaCl_2 : 21H_2O.$$

This result is in accord with the value $CaCl_2 : 22H_2O$ he had obtained by the sugar inversion method; in the case of other salts, a like agreement had been found. It was difficult to see how such agreements could be reconciled with the ionic dissociation hypothesis.

Dr. Philip said that it was certainly possible that hydrogen was soluble to some extent in chloral hydrate and sucrose, but it appeared unlikely in view of the fact that the average molecular hydration calculated on the basis of the two factors suggested in the paper agreed with values obtained by methods into which the question of solubility of hydrogen in these substances could not possibly enter.

The view that hydrates exist in aqueous solutions of electrolytes was not inconsistent with a general adherence to the ionic theory.

***65. "A new class of organo-metallic compounds. Preliminary notice. Trimethylplatinimethyl hydroxide and its salts." By William Jackson Pope and Stanley John Peachy.**

No alkyl compounds of metals belonging to group 8 of the periodic table have hitherto been described. The authors find that the chlorides, or in some cases the oxides, of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, belonging to group 8, and of gold, belonging to group 1, react vigorously

with magnesium methyl iodide; they desire to reserve the study of the action of Grignard's reagent on compounds of the metals named.

Trimethylplatinimethyl iodide, $(CH_3)_3PtI$, is formed by the action of platinic chloride dissolved in ether on magnesium methyl iodide in ethereal benzene solution; after treating with water and extracting with benzene, the benzene solution yields the new compound on evaporation. It crystallises in straw-yellow plates, is not volatile, and decomposes on heating with slight explosion; it is very stable towards reagents, and is not attacked in the cold by strong caustic alkalis, alkali sulphides, or by nitric, hydrochloric, and sulphuric acids. It is not further acted on by magnesium methyl iodide. On boiling for several hours with silver hydroxide in a moist mixture of benzene and acetone, it is converted into *trimethylplatinimethyl hydroxide*, $(CH_3)_3Pt{\cdot}OH$; this substance is insoluble in water, gives no alkaline reaction with litmus, and crystallises in colourless rhombic dodecahedra belonging to the cubic system.

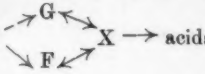
Trimethylplatinimethyl nitrate, $(CH_3)_3Pt{\cdot}NO_3$, obtained by dissolving the hydroxide in nitric acid, crystallises in colourless plates and is freely soluble in water. On adding an alkali chloride to its aqueous solution, *trimethylplatinimethyl chloride*, $(CH_3)_3PtCl$, is precipitated; this salt crystallises from chloroform in colourless, rhombic dodecahedra belonging to the cubic system. In a similar manner a number of other salts have been prepared, including the *bromide* and the *cyanide*; the latter is hydrolysed on heating with caustic potash with evolution of ammonia.

ISCUSSION.

The CHAIRMAN congratulated the authors on having opened out an entirely new branch of investigation which might indeed be said to be a wonderful "find."

66. "Some compounds of guanidine with sugars. Part I." By Robert Selby Morrell and Albert Ernest Bellars.

When an alcoholic solution of guanidine is added to dextrose, lævulose, mannose, arabinose, rhamnose, galactose, or maltose, dissolved in ethyl alcohol, white, microcrystalline precipitates are obtained. The general formula for dextrose-, lævulose-, and mannose-guanidine is $3C_6H_{12}O_6,2CN_3H_5$. In $N/2$ solutions, the compounds are dissociated into their components to the extent of 71 per cent. The depression of the freezing points of mixed dextrose and guanidine solutions was determined on the lines of H. Euler's researches (*Ber.*, 1905, **38**, 2551; 1906, **39**, 350), and the results confirm his view as to the acid character of carbohydrates in aqueous solution. The strength of

guanidine as a base compared with caustic soda was determined by (*a*) the saponification of ethyl acetate, (*b*) the velocity of fall in rotation angle of a hyoscyamine solution in the presence of guanidine (Will and Bredig, *Ber.*, 1888, **21**, 2777). The strengths of guanidine and caustic soda were found to be in the ratio of 0·8 : 1. Aqueous solutions of dextrose-, lævulose-, or mannose-guanidine show a gradual fall in optical rotation to a minimum value, which is the same for the three compounds. This behaviour is similar to that investigated by Lobry de Bruyn in the action of alkalis on sugars. The results obtained from the study of the mutarotation of solutions of dextrose-, lævulose-, or mannose-guanidine may be summarised as follows: (1) the fall in optical rotation to a constant minimum represents an apparent equilibrium in the case of dextrose- and lævulose-guanidine between two sugars through an intermediate substance X, the concentration of which is very small, $G \leftrightarrow X \leftrightarrow F$. (2) The velocity constants for the transformation of dextrose into lævulose, and *vice versâ*, were found to be 0·0015 and 0·0021 respectively; the velocity constants for the change of mannose into lævulose and dextrose are 0·0005 and 0·00036 respectively. The velocity of the reverse change of lævulose and dextrose into mannose is very small. (3) There is a slow disappearance of X, the intermediate substance, to form acids. When optical equilibrium has been reached, the ratio of lævulose to dextrose remains constant until the formation of acids ceases. The changes may be represented by the scheme 

67. "The action of aluminium chloride on naphthalene. Formation of ββ-dinaphthyl, tetranaphthyl, and tetramethylerythrene." By Annie Homer.

The action of aluminium chloride on naphthalene has been studied in detail. ββ-Dinaphthyl, $C_{20}H_{14}$, was formed, as had been indicated by Friedel and Crafts. Besides this compound, three new hydrocarbons were isolated, namely: (1) an oil, $C_{14}H_{16}$, probably *tetramethylnaphthalene*; (2) a resinous hydrocarbon, $C_{26}H_{22}$, to which the name *tetramethylerythrene* has been given; and (3) a yellowish-red solid, *tetranaphthyl*, $C_{40}H_{26}$.

Tetramethylerythrene is deep red, and its solutions, besides being highly fluorescent, show two absorption bands in the blue and violet portions of the spectrum respectively.

ββ-Dinaphthyl and tetranaphthyl are produced by condensation of the naphthalene molecules. The mode of formation of tetramethylerythrene is open to question.

68. "Mercurous hyponitrite." By Prafulla Chandra Rây.

The author has succeeded in preparing this salt in a purer form than that described in a former paper (*Trans.*, 1897, 71, 348). A solution of mercurous hyponitrite in nitric acid, unlike the silver salt, undergoes slow dissociation into mercury and mercuric hyponitrite.

69. "The decomposition of mercurous and silver hyponitrites by heat." By Prafulla Chandra Rây and Atul Chandra Gañguli.

The gaseous products of decomposition of mercurous hyponitrites are nitrogen, nitrogen monoxide, and nitrogen dioxide, the proportion of the first being very small.

Silver hyponitrite also yields the same gases with a much larger proportion of nitrogen dioxide. The authors are of opinion that these salts have both an oxylic and imidic constitution.

70. "Studies in optical superposition. Part III." By Thomas Stewart Patterson and John Kaye.

l-Menthyl diacetyl-*i*-tartrate has been prepared and its rotation has been determined both in the homogeneous state and in solution in ethyl alcohol, benzene, and nitrobenzene. The results, taken in conjunction with those previously published (*Trans.*, 1905, 87, 33; 1906 89, 1884), furnish for the first time thoroughly valid evidence as to the untenability of van't Hoff's assumption regarding optical superposition.

The following table exhibits this comparison at different temperatures for the homogeneous substances:

t°.	I. *l*-Menthyl diacetyl-*d*-tartrate.	II. *l*-Menthyl diacetyl-*l*-tartrate.	III. Mean of I and II.	IV. *l*-Menthyl diacetyl-*i*-tartrate.	Δ IV—III.
20°	−256°	−360°	−308°	−274°	34°
100	228	382	305	280	*l*
130	216	390	303	282	21

For solutions, the values found were as follows:

Solvent.	I. *l*-Menthyl diacetyl-*d*-tartrate.	II. *l*-Menthyl diacetyl-*l*-tartrate.	III. Mean of I and II.	IV. *l*-Menthyl diacetyl-*i*-tartrate.	Δ. IV—III.
Ethyl alcohol	−268° (*p* : 5)	−367° (*p* : 5)	−317·5°	−292° (*p* : 0·455)	25·5°
Benzene	285 ,,	313 ,,	299·0	248 (*p* : 5·2)	51·0
Nitrobenzene	238 ,,	355 ,,	296·5	244 (*p* : 4·38)	52·5

Both in the homogeneous condition and in solution therefore the rotation of the *i*-tartrate is markedly greater (that is, less negative)

than the means of the values for the *d*- and *l*-tartrates, and this furnishes conclusive evidence that the rotation due to a given asymmetric atom in a compound of two or more asymmetric radicles is not independent of the configuration of the other group or groups with which it is combined.

71. "An extension of the benzoin synthesis."
By Reginald William Lane Clarke and Arthur Lapworth.

Although mandelonitrile or its benzoyl derivative is too unstable to condense with $a\beta$-unsaturated ketones, yet its aniline derivative, benzylideneaniline hydrocyanide, can be made to do so.

With carvone, *phenylimino-β-benzoyldihydrocarvone* is obtained :

$$\begin{matrix}\mathrm{NHPh}\\\mathrm{CN}\end{matrix}\!\!>\!\mathrm{CHPh} + \mathrm{CH}\!<\!\begin{matrix}\mathrm{CMe}\\\mathrm{C_6H_{10}}\end{matrix}\!\!>\!\mathrm{CO} =$$

$$\mathrm{NPh{:}CPh{\cdot}CH}\!<\!\begin{matrix}\mathrm{CHMe}\\\mathrm{C_6H_{10}}\end{matrix}\!\!>\!\mathrm{CO} + \mathrm{HCN},$$

and this, on hydrolysis with acids, yields two stereoisomeric *β-benzoyldihydrocarvones.*

With benzylideneacetophenone, *γ-cyano-α-benzoyl-γ-anilino-βγ-diphenylpropane* is the product :

$$\begin{matrix}\mathrm{NHPh}\\\mathrm{CN}\end{matrix}\!\!>\!\mathrm{CHPh} + \mathrm{CHPh{:}CH{\cdot}CO{\cdot}Ph} =$$

$$\begin{matrix}\mathrm{NHPh}\\\mathrm{CN}\end{matrix}\!\!>\!\mathrm{CPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO{\cdot}Ph},$$

the constitution of which was shown by converting it by heat into water, hydrogen cyanide, and tetraphenylpyrrole, $\mathrm{NPh}\!<\!\begin{matrix}\mathrm{CPh{:}CH}\\\mathrm{CPh{:}CPh}\end{matrix}$.

In neither instance does benzylideneaniline alone afford any analogous products. These condensations were shown to be extensions of the well-known "benzoin synthesis" as interpreted by one of the authors (*Trans.*, 1903, **83**, 1004).

72. "Interaction of starch and carbon disulphide. Xanthogenic esters of starch." By Charles Frederick Cross, Edward John Bevan, and John Frederick Briggs.

Alkali starch in its hydrated forms is a gelatinous impenetrable mass which is only superficially attacked by carbon disulphide.

Starch moistened with the disulphide and then treated with a sodium hydroxide solution (15 to 20 per cent.) is brought into the condition for quantitative reaction and conversion into the xanthogenic ester (sodium salt). The derivatives are analogous in all respects to those of cellulose (*Trans.*, 1893, **63**, 837).

73. "The estimation of small quantities of nitrogen peroxide." By Robert Robertson and Sidney Scrivener Napper.

The method depends on the changes observed in the characteristic absorption spectrum of nitrogen peroxide as its concentration in dilute mixtures is increased. It was found that a few of the more prominent groups of lines were visible at a concentration of 0·05 per cent. nitrogen peroxide, and that as the proportion was raised the lines increased in intensity and number until the violet end of the spectrum was completely absorbed in mixtures approaching a concentration of 1·0 per cent. These differences are sufficiently well marked to enable a process to be worked out for the quantitative estimation of the concentration by comparison with standard mixtures. Photographic comparison was employed, and for this purpose a series of standard photographs covering a range of concentration from 0·05 to 1 per cent. was prepared.

The method when applied to the estimation of small quantities of nitrogen peroxide in air gives very satisfactory results, and the process which is applicable to any gaseous mixture has been used successfully for the investigation of the gases evolved during the slow decomposition of guncotton.

74. "The evolution of nitrogen peroxide in the decomposition of guncotton." By Robert Robertson and Sidney Scrivener Napper.

Previous investigators have given accounts of experiments in which guncotton was slowly decomposed at temperatures near 130° in a vacuum and in a current of carbon dioxide, and have stated that only a small quantity of nitrogen peroxide was evolved, or have made no reference to its presence. With the help of the method described by the authors (compare preceding paper) a careful study has been made of the gases given off by guncotton when heated under various conditions.

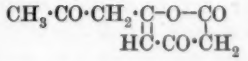
These include heating (1) in a vacuum; (2) in a stream of carbon dioxide; (3) in an unchanged atmosphere of carbon dioxide; (4) in nitrogen dioxide, and (5) in air. In all cases more than 10 per cent. of the total nitrogen evolved was in the form of nitrogen peroxide, and a study of the results shows that the proportion is largely dependent on the conditions of experiment; the deposition of water and prolonged contact with the heated guncotton tend to reduce it, and when these two conditions are not present the proportion rises to 40—50 per cent. This occurs when the guncotton is heated under the conditions of the Will test, and reduction of the rate of the current of carbon dioxide

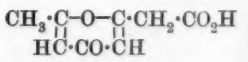
causes a reduction of the proportion of nitrogen peroxide evolved. This effect is apparently due to the action of the nitrogen peroxide on the guncotton, and is accompanied by a rise in the total amount of nitrogen evolved, indicating that oxides of nitrogen cause an increase in the rate of decomposition of guncotton.

75. "An isomeric change of dehydracetic acid." By John Norman Collie and Thomas Percy Hilditch.

During the preparation of a large quantity of triacetic lactone, it has been noticed that if sulphuric acid of about 85 per cent. instead of about 90 per cent. is allowed to act on dehydracetic acid, the yield of triacetic lactone is much diminished. On pouring the product into water, an acid, $C_8H_8O_4$, isomeric with dehydracetic acid, has been separated. It has a molecular weight of 169, is a true acid, not a lactone, melts at 99°, and has an electrical conductivity $k = 0{\cdot}00152$. When heated to about 200° it is converted almost quantitatively into carbon dioxide and dimethylpyrone. On boiling with excess of strong solution of barium hydroxide it yields barium acetate, acetone, and barium malonate. A solution of the neutral sodium salt on boiling is converted into sodium dehydracetate, from which dehydracetic acid is precipitated by adding an acid.

The free acid, when heated with an excess of ammonia, gives the ammonium salt of a lutidonecarboxylic acid. This acid, $C_8H_8O_4$, seems to agree in all respects, except its electrical conductivity, with an acid obtained by Feist (*Annalen*, 1890, **257**, 253), and is a true pyronecarboxylic acid :


Dehydracetic acid.


Pyronecarboxylic acid.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Rey, *Jean.* Essais de Jean Rey. Édition nouvelle avec commentaire, publiée par *Maurice* **Petit.** pp. xxviii + 192. Paris 1907. (*Recd.* 13/3/07.) From the Publisher: A. Hermann.

Robertson, *Frederick D. S.* Practical agricultural chemistry. A manual of qualitative and quantitative analysis for agricultural students. pp. x + 210. ill. London 1907. (*Recd.* 13/3/07.) From the Publishers: Messrs. Baillière, Tindall, and Cox.

Sommerfeldt, *Ernst.* Physikalische Kristallographie vom Standpunkt der Strukturtheorie. pp. vii + 132. ill. Leipzig 1907. (*Recd.* 13/3/07.) From the Publisher: C. H. Tauchnitz.

Thoms, *H.* Ueber Mohnbau und Opiumgewinnung. pp. 60. ill. Berlin 1907. (*Recd.* 13/3/07.)

II. *By Purchase.*

Deutsches Bäderbuch, bearbeitet unter Mitwirkung des Kaiserlichen Gesundheitsamtes. pp. [viii] + civ + 535. Leipzig 1907. (*Recd.* 20/3/07.)

Tammann, *G.* Ueber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen. Ein Beitrag zur Theorie homogener Systeme. pp. viii + 184. Hamburg 1907. (*Recd.* 20/3/07.)

Tappeiner, *H. v.*, und **Jodlbauer,** *A.* Die sensibilisierende Wirkung fluorescierender Substanzen. Gesammelte Untersuchungen über die photodynamische Erscheinung. pp. viii + 210. ill. Leipzig 1907. (*Recd.* 20/3/07.)

ERRATUM.

1907. P. 74, line 15 from top, *for* "**Cohen**" *read* '**Cahen.**"

At the next Ordinary Meeting on Thursday, April 18th, 1907, the following papers will be communicated:

"The magnetic rotation of hexatriene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, and its relationship to benzene and other aromatic compounds, also its refractive power." By Sir W. H. Perkin.

"Aromatic azoimides. Part I. *p*-Hydroxyphenylazoimide." By M. O. Forster and H. E. Fierz.

"The action of hydrogen peroxide on potassium cyanide." By O. Masson.

"The action of ethyl oxalate on thioacetanilide and its homologues." By S. Ruhemann.

"Measurements of the velocities of saponification of the *l*-menthyl and *l*-bornyl esters of the stereoisomeric mandelic acids." By A. McKenzie and H. B. Thompson.

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Issued 29/4/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 324.

Friday, 22nd March, 1907. Annual General Meeting, Professor R. MELDOLA, F.R.S., President, in the Chair.

Dr. G. D. Lander and Dr. J. F. Thorpe were appointed scrutators and the Ballot was opened for the election of Officers and Council for the ensuing year.

The PRESIDENT presented the Report of the Council on the progress of the Society during the past twelve months. The adoption of the Report of the Council was proposed by Prof. J. B. Harrison, seconded by Prof. W. Jackson Pope, and carried unanimously.

REPORT OF THE COUNCIL.

THE Council has the satisfaction of being able to report the continued prosperity of the Society and that, measured by the number of papers read and the number of Fellows on the list, there has been greater activity than in any previous year.

On the 31st December, 1905, the number of Fellows was 2,785. During 1906, 172 Fellows were elected and 2 reinstated, thus making a gross total of 2,959. The Society has lost 24 Fellows by death; 24 have resigned, the elections of 5 have become void; 39 have been removed for non-payment of Annual Subscriptions, and 7 Life Compounders, whose addresses could not be found, have been removed.

The total number of Fellows, therefore, on the 31st December, 1906, was 2,860, showing an increase of 75 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:

W. H. Chandler (1872).
F. J. Claudet (1852).
T. S. Davis (1876).
W. H. Edwards (1902).
M. H. Foye (1884).
C. H. B. Hambly (1859).
J. G. Hepburn (1853).
J. S. C. Heywood (1848).
G. H. Hurst (1885).
F. M. Lyte (1859).
C. W. Marsh (1881).
E. H. Miller (1897).
W. J. Orsman (1884).
B. Phillips (1889).
J. E. Pitman (1906).
T. Royle (1862).
F. Smith (1890).
T. D. Smith (1898).
H. J. P. Sprengel (1864).
W. S. Squire (1858).
J. A. Storey (1891).
C. Tookey (1855).
T. B. Tyson (1885).
A. Walker, Maj-Gen. (1868).

The following Fellows have resigned:

G. D. Atkinson.
J. Bateman.
W. C. T. Beasley.
Sir B. V. S. Brodie, Bt.
C. H. Burge.
J. M. Campbell.
H. E. Ellis.
J. C. Fell.
P. Haigh.
S. M. Haigh.
W. Harris.
E. Hughes.
R. B. Lee.
H. L. Leech.
H. P. Lewis.
W. C. Mackenzie.
A. S. Mayfield.
J. B. Moody.
J. W. Sandford.
G. T. S. Sichel.
W. H. Sodeau.
R. C. Styles.
G. E. Tomlins.
P. J. Vinter.

The names of the Life Compounders whose addresses cannot be found, and who have been removed therefore by the Council, are:

G. Crampton (1875).
J. Danson (1850).
A. A. Ferreira (1864).
A. W. Gillman (1865).
J. Hadkinson (1878).
F. E. Harman (1874).
James Millar (1848).

The number of the Fellows who were elected in the early part of the last century has been still further diminished by the death of Mr. F. J. Claudet, elected on 16th February, 1852; Mr. J. G. Hepburn, elected on 21st February, 1853; and of Mr. J. S. C. Heywood, who was elected on 3rd April, 1848.

The number of Honorary and Foreign Members at the close of 1905 was 34. No elections have been held during 1906, but the Society has to mourn the loss of Dr. Fedor Beilstein, who was elected

1st February, 1883, and who died on 19th October, 1906. The number of Honorary and Foreign Members at 31st December, 1906, was therefore 33.

Since the close of 1906, the Society has lost by death three more of its Honorary and Foreign Members, namely, Prof. Dr. D. I. Mendeléeff, (on 2nd February), Prof. Dr. Nicolai Menschutkin (on 4th February), and Prof. Henri Moissan (on 20th February).

During the year 1906, 236 scientific communications have been made to the Society, 176 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of Transactions for 1906 contains 1,943 pages, of which 1,890 are occupied by 186 memoirs, the remaining 53 pages being devoted to the Cleve Memorial Lecture, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 184 memoirs, which occupy 1,818 pages.

The Journal for 1906 contains also 4,541 abstracts of papers published mainly in foreign journals, which extend to 1,912 pages, whilst the abstracts for 1905 numbered 4,356, and occupied 1,828 pages.

The abstracts for 1906 may be classified as follows:

Part I.

	Pages.	No. of Abstracts.
Organic Chemistry	1,000	1,745

Part II.

General and Physical Chemistry		651
Inorganic Chemistry		559
Mineralogical Chemistry		128
Physiological Chemistry		486
Chemistry of Vegetable Physiology and Agriculture		343
Analytical Chemistry		629
	912	2,796
Total in Parts I. and II.	1,912	4,541

Among the first acts of the Council elected in March, 1906, was the appointment of a Finance Committee, and it was decided also that the names of the Members, together with those of the House, Library, Publication, and Research Fund Committees, should be read from the Chair at the Ordinary Meeting next after the Meeting of Council at which the Committees are formed.

In the previous session, and on a second occasion during the present one, the desirability of reading the minutes at an Ordinary Meeting has been called in question; for the guidance of Chairmen on this point it has been resolved that henceforth the minutes must be read as long as the present Bye-Laws remain in force.

The practice of holding the Ordinary Meetings of the Society on the first and third Thursdays of the month, reversion to which was announced in the last Annual Report, appears justified by the average attendance of Fellows, which has been well maintained. In order to relieve the pressure of business which has been usual at the first and last Meetings of the Session, it was decided to hold two extra Meetings, in October and July respectively.

The triennial award of the Longstaff Medal to the Fellow of the Society who, in the opinion of the Council, has done the most to promote Chemical Science by Research, was made, on the recommendation of the Research Fund Committee, to Prof. Walter Noel Hartley, F.R.S., in recognition of his spectrochemical investigations. The medal was presented on October 18th, 1906.

On the occasion of the International Celebration marking the Fiftieth Anniversary of the Foundation of the Coal Tar Colour Industry, an address of congratulation to Sir William Henry Perkin, F.R.S., was presented on behalf of the Society by the President. In accordance with the resolution of the public meeting at which the commemoration was inaugurated, a marble bust of Sir William Perkin, executed by Mr. F. W. Pomeroy, A.R.A., has been presented to the Society by the Committee administering the Fund subscribed in support of the celebration.

The Society has also received a Berzelius medal cast in selenium, presented by Mr. John Spiller, and Prof. J. M. Thomson, F.R.S., has presented an aqua-tint engraving of Dr. Thomas Thomson, F.R.S., Regius Professor of Chemistry in the University of Glasgow from 1818 to 1852.

During the vacation of 1906 an address was presented to the University of Aberdeen at the celebration of its fourth centenary, which took place in September. The congratulations of the Society were offered also to the distinguished Honorary and Foreign member, Professor Adolph Lieben, on the occasion of his seventieth birthday and fiftieth anniversary of his doctorate.

The desirability of applying for a supplemental Charter with a view to removing existing restrictions in regard to nationality and sex as affecting election to the Fellowship of the Society has been carefully considered by the Council. After receiving the report of a Special Committee consisting of Mr. Phipson Beale, Mr. Bousfield, Dr. Horace Brown, Dr. Moody, Professor Emerson Reynolds, Dr. T. E. Thorpe,

Professor W A. Tilden, and the Officers, the Council resolved that for the guidance of Chairmen, only those Fellows who are British subjects can vote at meetings or be eligible for offices, and that the matter be made clear by adding to the gloss on the Charter, after the first paragraph, the words "but British subjects who are Fellows can alone exercise corporate rights, or be eligible for office."

The Council has resolved that, following the ordinary index of the Transactions, there shall appear a list of new compounds described in the original communications, tabulated according to the Richter system.

The alchemical and early chemical works presented to the Library by Sir Henry E. Roscoe have been catalogued (Proc., 1906, 22, 209—233) and the volumes placed in a special book-case.

The number of books borrowed from the Library during 1906 was 1,126, as against 1,108 in the previous year. The additions to the Library comprise: (*a*) a collection of 136 alchemical and other books presented by Sir Henry E. Roscoe; (*b*) 121 books, of which 64 were presented, 385 volumes of periodicals, and 32 pamphlets, as against 165 books, 324 volumes of periodicals, and 48 pamphlets last year.

In January last the Council decided that during the remainder of the present Session the Library shall be kept open for the use of Fellows every Thursday from 10 a.m. until 9 p.m., except on those evenings on which the Society meets, when it will remain open until 10.30 p.m.

The annual income of the Research Fund from its investments is £219 17*s.* 0*d.*, and from this grants amounting to £210, as well as the Longstaff Honorarium and Medal, had to be paid. That this should be not only possible, but that there should also be an excess of income over expenditure of £26 13*s.* 11*d.* for the year, is due to the amount of £38 6*s.* 11*d.* having been returned from grants made in previous years. In the Transactions for 1906 there are 31 papers contributed by authors to whom grants had been made from the Research Fund.

The Treasurer has great pleasure in recording that in February of the present year the Society received a further munificent donation of £1,000 to the Research Fund from the Worshipful Company of Goldsmiths. The income accruing from this donation will, in accordance with the expressed wish of the donors, be devoted especially to the encouragement of research in metallurgy and inorganic chemistry.

The financial transactions of the Society for the past year have been very satisfactory and show a substantial surplus. The total income of the Society for 1906 is £7,121 8*s.* 11*d.*, being an increase of £327 14*s.* 11*d.* over that for 1905 (£6,793 14*s.* 0*d.*), in spite of the fact that the amount received on account of Life Composition Fees has fallen from £360 to £268, a decrease of £92. The increase in

income is mainly composed of the following three items: (1) admission fees, £120; (2) annual subscriptions, £138 18*s.* 0*d.*; and (3) sale of publications, £120 6*s.* 3*d.* Whilst the income has notably increased, the expenditure has fallen much more considerably and is £718 19*s.* 8*d.* less than last year, so that instead of a deficit of £305 1*s.* 5*d.* on the year's working there is a surplus of £741 13*s.* 2*d.*, a difference in all of £1,046 14*s.* 7*d.* This is due very largely to having no expenses of any kind to meet on account of the Collective Index, which last year alone cost the Society £778 10*s.* 5*d.*, but it must not be thought that nothing is being done towards the preparation of the next volume, because the card indexes now made by Mrs. Dougal for each Annual Index will, with comparatively little expense and labour, be blended together and thus utilised for the preparation of Vol. V. of the Collective Index, which will cover the period 1903—1912.

The cost of the *Journal*, the *Proceedings*, and the *Annual Reports* all show increased expenditure, amounting to £71 7*s.* 6*d.*, £40 6*s.*, and £68 10*s.* 7*d.* respectively. It is very satisfactory to notice that although the Transactions and Abstracts show an increase of over 200 pages and contain several lengthy, as well as important and expensive, papers, the increase in cost should be so small. In this connexion the Treasurer has to thank Professor Pope and Mr. Barlow for supplying all the blocks required to illustrate their paper published in the November issue of the *Journal*. The increased cost of the Proceedings is due in part to the issue of two additional numbers corresponding to the two extra Meetings of the Society in July and in October, and in part also to the printing of the catalogue, compiled with great care by the Librarian, of the collection of alchemical works above referred to which the Society owes to the generosity of Sir H. E. Roscoe, and which are now properly housed in the Library.

The balance sheet also shows that a small legacy of £33 12*s.* 3*d.* has been received under the will of the late Mr. Henry Dircks, and is a residue of the estate from which almost exactly thirty years ago the Society received £840 5*s.*

The Treasurer gave a statement as to the Society's Income and Expenditure during the year 1906, and proposed a vote of thanks to the Auditors, which was seconded by Dr. W. R. E. Hodgkinson and carried unanimously. Acknowledgment was made by Mr. E. Grant Hooper.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Sir William H. Perkin, seconded by Dr. E. Divers, and adopted unanimously; this was acknowledged by Sir William Ramsay.

The President then delivered his address, entitled "The Position and Prospects of Chemical Research in Great Britain." Dr. T. E. Thorpe proposed a vote of thanks to the President coupled with the request that he would allow it to be printed in the Society's *Transactions*. The motion was seconded by Prof. J. Millar Thomson, and carried with acclamation, the President making acknowledgment.

The Scrutators then presented their report to the Chairman, who declared that the following had been duly elected as Officers and Council for the ensuing year:

President: Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the Office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; Sir W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: J. J. Dobbie, M.A., D.Sc., F.R.S.; Rudolph Messel, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D., F.R.S.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary: Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council: Edward C. C. Baly; George T. Beilby, F.R.S.; Bernard Dyer, D.Sc.; W. R. E. Hodgkinson, Ph.D.; E. Grant Hooper; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; G. T. Moody, D.Sc.; A. G. Perkin, F.R.S.; W. J. Sell, D.Sc., F.R.S.; John Wade, D.Sc.

ANNIVERSARY DINNER.

The Anniversary Dinner of the Society was held at the Whitehall Rooms on Friday, March 22nd, at 7 p.m., at which the following Fellows and Guests were present:

Armit, Dr. H.
Armstrong, Dr. E. F.
Armstrong, Prof. H. E., F.R.S., *Past President.*
Baker, Dr. H. B., F.R.S.
Baker, Mr. J. L.
Barger, Dr. G.
Barry, Sir John Wolfe, K.C.B., F.R.S., *Chairman of Executive Committee, City and Guilds of London Institute.*
Bayliss, Dr. W. M., F.R.S.
Beale, Mr. W. P., K.C., M.P.
Beilby, Mr. G. T., F.R.S.
Blaikie, Mr. L.
Brewin, Mr. A., *Prime Warden, The Dyers' Company.*
Briggs, Mr. H.
Brown, Prof. A. J.
Brown, Dr. H. T., F.R.S., *Vice-President, and Foreign Secretary-elect.*
Brunton, Sir T. Lauder, F.R.S.
Cain, Dr. J. C., *Editor.*
Carpmael, Mr. W.
Carr, Mr. S. E., *Assistant Secretary.*
Carvalho, Mr. S. N.
Chapman, Mr. A. C.
Clark, Dr. John, *President, The Society of Public Analysts.*
Clifford, Mr. F. W., *Librarian.*
Clowes, Prof. F.
Coburn, Mr. H. I.
Cockburn, Hon. Sir John A., K.C.M.G.
Colman, Dr. H. G.
Cooper, Mr. A.
Cooper, Dr. H. C.
Crossley, Prof. A. W., *Hon. Secretary.*
Daily Telegraph, The
Dale, Dr. H. H.
Desch, Dr. C. H., *Assistant Sub-Editor.*
Divers, Prof. E., F.R.S.
Dixon, Prof. H. B., F.R.S., *Vice-President.*
Dixon, Prof. W. E.
Dobbie, Prof. J. J., F.R.S., *Vice-President-elect.*
Dyer, Dr. B.
Elliott, Sir T. H., K.C.B., *Secretary, The Board of Agriculture.*
Elliott, Mr. T. R.
Ewing, Prof. J. A., F.R.S., *Director of Naval Education.*
Fairley, Mr. T.
Farmer, Prof. J. B., F.R.S.
Feilmann, Dr. M. E.
Fenton, Dr. H. J. H., F.R.S.
Fierz, Dr. H. E.
Finzi, Mr. J. A.
Fischer, Geh. Rath Prof. Dr. E., F.R.S.
Fisk, Mr. F. M.
Forbes, Mr. F. A.
Forster, Dr. M. O., F.R.S., *Hon. Secretary.*
Friswell, Mr. R. J.
Gabriel, Geh. Rath Prof. Dr. S.
Gardner, Mr. H. C. T.
Geikie, Sir A., F.R.S., *President, The Geological Society.*
Gibbons, Mr. W. M.
Glazebrook, Dr. R. T., F.R.S., *President, The Institution of Electrical Engineers.*
Green, Prof. A. G.
Greenaway, Mr. A. J., *Sub-Editor.*
Greenish, Prof. H. G.
Hall, Mr. S.
Hall, Mr. S. G.
Harden, Dr. A.
Hardy, Mr. W. B., F.R.S.
Harrison, Prof. J. B., C.M.G.
Harvey, Dr. J. S.
Henry, Dr. T. A.
Hewitt, Dr. J. T.
Heycock, Mr. C. T., F.R.S.
Hill, Mr. C. A.
Hodgkinson, Prof. W. R. E.
Holloway, Mr. G. T.
Hooper, Mr. E. G.
Hopkins, Dr. F. G., F.R.S.
Humphrey, Mr. J.
Jones, Dr. H. O.
Jowett, Dr. H. A. D.
Kelvin, Rt. Hon. Lord, O.M., G.C.V.O., F.R.S.
Kemp, Mr. W. J.
Kipping, Prof. F. S., F.R.S.
Lankester, Prof. E. Ray, F.R.S., *President, The British Association for the Advancement of Science.*
Lees, Mr. F. H.
Le Sueur, Dr. H. R.
Lewkowitsch, Dr. J.
Lockyer, Sir J. N., K.C.B., F.R.S. *Chairman of Committee, British Science Guild.*
Lowry, Dr. T. M.
Luard, Mr. S. W., *Clerk, The Salters' Company.*
Lunge, Prof. Dr. G.
Maben, Mr. T.

MacEwan, Mr. P.
McGowan, Dr. G.
MacMahon, Major P. A., R.A., F.R.S.
Mander, Mr. G. Le M.
Marsh, Mr. J. E., F.R.S.
Martin, Sir Richard B., Bart., *Prime Warden, The Fishmongers' Company.*
Matthews, Dr. F. E.
Meldola, Prof. R., F.R.S., *The President.*
Messel, Dr. R., *Vice-President.*
Mohr, Dr. B.
Mondy, Mr. E. F.
Moody, Dr. G. T.
Morant, Mr. R. L., C.B., *Permanent Secretary, The Board of Education.*
Morning Post, The
Morrell, Dr. R. S.
Morris, Mr. H., *President, Royal College of Surgeons.*
Moseley, Mr. A., C.M.G.
Moss, Mr. C. C. B.
Müller, Dr. Franz.
Müller, Dr. H., F.R.S., *Past President.*
Nagel, Mr. D. H.
Nathan, Lt.-Col., Sir F. L., R.A., *Superintendent, Royal Gunpowder Factory, Waltham Abbey.*
Ogilvie, Mr. F. G., *Princ. Assist. Secretary, Technology and Higher Education in Science and Art, Board of Education.*
Orton, Prof. K. J. P.
Page, Mr. F. J. M.
Palmer, Sir W., Bart.
Paterson, Mr. J. B.
Pedler, Sir A., C.I.E., F.R.S., *Vice-President-elect.*
Perkin, Prof. A. G., F.R.S.
Perkin, Sir W. H., F.R.S., *Past President.*
Perkin, Prof. W. H., F.R.S. *Vice-President.*
Perry, Prof. J., F.R.S., *President, The Physical Society.*
Phené, Dr. J. S., *Master, The Clothworkers' Company.*
Plimmer, Dr. R. H. A.
Pope, Prof. W. J., F.R.S.
Poulton, Prof. E. B., F.R.S.
Power, Dr. F. B.
Prain, Lt.-Col. D., F.R.S., *Director, Royal Botanic Gardens, Kew.*
Press Association, The
Prideaux, Sir W. S., *Clerk, The Goldsmiths' Company.*
Pugh, Mr. A. J.
Ramsay, Sir W., K.C.B., F.R.S., *Foreign Secretary and President-elect.*
Ransford, Mr. R. B.
Rayleigh, Rt. Hon. Lord, O.M., F.R.S., *President, The Royal Society.*
Rees, Mr. H. P.
Reynolds, Prof. J. E., F.R.S., *Past President.*
Roberts, Sir O., *Clerk, The Clothworkers' Company.*
Rücker, Sir A. W., F.R.S., *Principal, The University of London.*
Ruhemann, Dr. S.
Russell, Dr. W. J., F.R.S., *Past President.*
Ryan, Prof. F.
Salamon, Mr. A. G., *President, Institute of Brewing.*
Samuel, Mr. H., M.P., *Parliamentary Under Secretary of State for the Home Department.*
Scott, Dr. A., F.R.S., *Treasurer.*
Seligman, Dr. R.
Sell, Dr. W. J., F.R.S.
Silberrad, Dr. O.
Smith, Dr. F. H.
Smithells, Prof. A., F.R.S., *Vice-President*
Soper, Mr. A. L.
Spielmann, Mr. M. H., F.S.A.
Spielmann, Mr. P. E.
Standard, The
Starling, Prof. E. H., F.R.S.
Stone, Sir B., M.P.
Streatfeild, Mr. F. H.
Streimer, Mr. E. G.
Strutt, Hon. R. J., F.R.S.
Sutton, Mr. G. F., *Clerk, The Dyers' Company.*
Swan, Sir J. W., F.R.S.
Thompson, Prof. S. P., F.R.S., *Principal, Finsbury Technical College.*
Thomson, Prof. J. M., F.R.S.
Thorpe, Dr. J. F.
Thorpe, Prof. T. E., C.B., F.R.S., *Past President.*
Tilley, Mr. J. W.
Tilley, Mr. V. J.
Times, The
Townshend, Col. G. R.
Tunnicliffe, Prof. F. W.
Tyrer, Mr. T., *President, The Pharmaceutical Conference.*
Vincent, Dr. J. H.
Wade, Dr. J.
Walker, Mr. J. T. A.
Waller, Dr. A.D., F.R.S.
Warren, Mr. T. H., *Vice-Chancellor, The University of Oxford.*
Weizmann, Dr. C.
West, Dr. S.
White, Sir W. H., K.C.B., F.R.S.
Woodcock, Mr. R. C.
Wynne, Prof. W. P., F.R.S., *Vice-President.*
Yarrow, Mr. A. F.
Young, Dr. G.
Zilz, Mr. H.

The following toasts were proposed:

By the President.

1. **His Most Gracious Majesty the King.**

2. **Her Majesty the Queen Alexandra, their Royal Highnesses the Prince and Princess of Wales, and the other Members of the Royal Family.**

By the Right Honourable Lord Rayleigh, O.M., F.R.S.,
President of the Royal Society.

3. **The Chemical Society,** coupled with the name of *The President.*

By Sir William Ramsay, K.C.B., F.R.S.,
President-Elect of the Chemical Society.

4. **Scientific Societies,** coupled with the names of the Right Honourable Lord Kelvin, O.M., G.C.V.O., F.R.S., and Professor E. Ray Lankester, F.R.S., *President of the British Association for the Advancement of Science.*

By Professor Henry E. Armstrong, F.R.S.,
Past President of the Chemical Society.

5. **Education,** associated with the names of Mr. T. H. Warren, *Vice-Chancellor of the University of Oxford;* Sir Arthur W. Rücker, F.R.S., *Principal of the University of London;* and Sir John Wolfe Barry, K.C.B., F.R.S., *Chairman of the Executive Committee of the City and Guilds of London Institute.*

Professor T. E. Thorpe, C.B., F.R.S.,
Past President of the Chemical Society.

6. **The Guests,** coupled with the names of Geh. Rath Professor Dr. Emil Fischer, F.R.S., and Professor J. A. Ewing, F.R.S., *Director of Naval Education.*

After the President had given the Loyal Toasts, The Right Honourable Lord Rayleigh, O.M., proposed The Chemical Society.

He said the toast would require but little commendation from him in such a company as was assembled. Although most of his time had been given up to the study of physics, he had always taken the keenest interest in their science, and at an early age had served a sort of apprenticeship to it, having managed to burn his fingers rather seriously with phosphorus before he was thirteen. Their science was so extensive and grew with such rapidity that many of its branches were but little known to him. As examples of this growth, he referred to the development of the aniline dye industry, which had become of immense theoretical and practical importance, and to the various branches so intimately connected with the name of Dr. Emil Fischer. In some aspects, chemistry might be regarded as a branch of physics, and only lately he had been looking over those wonderful papers of Willard Gibbs which were still the foundation of that branch of chemical science, and which had recently been collected and republished.

Prof. Meldola was a man of many and varied attainments. Primarily he was a chemist, but there were few departments of science with which he was not connected, and therefore in giving the toast of the Society he would couple with it the name of its President.

The President said he was deeply indebted to those present for the very kind reception which they had given to the toast proposed by the distinguished President of the Royal Society. He could not help feeling that this was one of those rare occasions that fall to the lot of the official representative of one of the scientific societies to speak to a somewhat wider public than his own immediate circle of colleagues who meet within the walls of the scientific societies, and he would take this opportunity of saying a word or two as to the work of these societies. He feared there was only too much truth in the accusation that this is an unscientific nation. Still, he would have it known that in societies like that assembled and in kindred societies there were banded together small armies of ardent workers who were keeping alight the torch of scientific research, and that, however unscientific nationally, when the time of scientific enlightenment arrived he hoped this would count to our credit and for merit. With regard to the Chemical Society in particular, he felt disposed to join issue with Lord Rayleigh as to whether chemistry should be regarded as a branch of physics or physics as a branch of chemistry. He claimed that in its ultimate association with other departments of science, chemistry was as far-reaching, as cosmopolitan, as any branch of science which was being cultivated at the present time. The Chemical Society was in an exceedingly flourishing condition. It was

a venerable Society, founded in 1841, and granted a Charter in 1848. It had therefore arrived at what, according to the Civil Service estimates, would be considered as the year of dotage, instead of which he regarded it as only just entering its prime. During the last few months the Society's ranks had been thinned by the hand of death in the most lamentable way. All its honorary and foreign Russian members, Beilstein, Mendeléeff, and Menschutkin, had been lost, and in France Moissan had passed away, and, quite recently, Berthelot. He was sure those assembled would like it to be known how deeply they sympathised with their foreign *confrères* on the international loss which science had sustained by the death of these distinguished chemists. The Society had a membership of nearly 2,900, and was spending from £4,000 to £5,000 a year in printing and publishing the Transactions, Proceedings, and Annual Reports. Of the value of these publications he need say nothing, for they were sufficiently well known, and if any justification for the Society's existence were ever needed its publications might be pointed out as the one great work which it had so successfully carried on. The editorial department was omnivorous. In the pages of the Journal, room was made for atoms and electrons, and even corpuscles. They all received perfectly impartial editorship, and if the new President would forgive the reference, space was even found for organic chemistry! Among the self-imposed duties of the President was the delivery of an annual address, and that afternoon he had been dealing with a subject he had closely in mind, namely, the position of chemical research in this country. He had come to the conclusion that there was an immense deal of chemical talent, of chemical faculty, but that there was an enormous wastage going on all over the country owing to unfavourable conditions, some of which he had endeavoured to analyse in the course of his address. That was a very deplorable state of affairs, for which he saw no immediate prospect of any remedy. He thought gratitude should be expressed for any checks to this wastage that might be in existence, and that it was the duty, not only of the Chemical Society as regards its own science, but the duty of the scientific world as a whole to give recognition to those agencies which were at work, helping to check this wastage of what he and many others considered to be one of the most valuable assets possessed by the country, namely, the original faculty of scientific work. Of such agencies he would mention the 1851 Exhibition Scholarship, the Fellowship given by the Salters' Company, and the Carnegie Scholarships. As to Research funds, the Government made a grant to the Royal Society, but Chemistry could only come in for its share along with other sciences. Then there was the Research Fund of the Chemical Society, from which there accrued the modest

income of some £220 per annum, and on account of that income being so modest its allotment had to be limited to workers for the purchase of expensive materials and apparatus. The fund had been augmented recently by the munificence of the Goldsmiths' Company, who had added £1,000 to it. He would take this public opportunity of expressing the appreciation of the whole scientific world at the munificence of this same Company, which had so splendidly endowed the Lawes Agricultural Institute by a gift of £10,000. Then it was hoped that in a short time the sum of £2,700 would be added to the Research Fund of the Chemical Society in the name of a distinguished past-President, Sir W. H. Perkin. Much more could be done if there were greater reserves to fall back upon. It had always been a point of ambition to him to see the Research Fund in such a position as would enable the Society to give personal grants to workers, so that they could each secure the services of competent men to co-operate with them in their work. That point appealed particularly to teachers like himself. All teachers had had brilliant young men passing through their classes who had been compelled to go out into the world as soon as possible to earn their living, and thus the country had practically lost the benefit of their capabilities. If by some such endowment as that alluded to teachers were enabled to capture talent of this kind and keep it going, the chemical research of the country would be an enormous gainer in the long run.

Sir Wm. Ramsay, K.C.B., proposed "Scientific Societies." After mentioning many of the learned Societies of Europe and America, he asked why were they banded together. There were important reasons. One was that the young members were enabled to meet the old, which gave great encouragement to the younger men, and their elders found pleasure in knowing them, but the chief reason was that they all had at heart the advancement of knowledge. They desired to increase the sum total of the knowledge of the phenomena of the world. Their desire to know was insatiable, and they were willing to make sacrifices to that end. In that way they founded a brotherhood with all others who were working like themselves, independent of politics and independent of nationality. For these reasons, he asked them to drink the toast.

Lord Kelvin, O.M., G.C.V.O., was the first to respond. He said he found it very difficult to distinguish between the scientific societies for which he had to reply. He believed "Physics" was the subject for which he was specially responsible. But chemistry—how was it distinguished from physics? For fifty-three years he had endeavoured to teach natural philosophy, which was Scotch for physics, and he never could distinguish between physics and chemistry. Well, what

was physics and what was chemistry? He would define them together as the science of Force. They heard much at present of the breaking up of atoms, but when they heard of an object from which something had been chipped, it could not have been an atom. He had read in the newspapers of the death-bed of an atom, and yet chemists were going to be told that there was no such thing as an atom! Whether there were many atoms of a different kind was a matter for investigation, but whether each atom of its own kind remained for ever unchanged or not was a subject much discussed. He was not then going to give an opinion upon it, but it was better not to call a thing an atom when it was broken. As to chemistry, he had great sympathy with it. Lord Rayleigh burnt his fingers with phosphorus when he was thirteen. Well, he (Lord Kelvin) had burnt his fingers with phosphorus when he was eighty-two, a thing but few chemists or physicists could say.

Prof. E. Ray Lankester also responded. Scientific societies at the present time were somewhat limited in their objects, or at any rate in their possible activity. He thought they should become something more like the ancient guilds of the great cities of Europe, and endeavour to obtain large funds from those who had benefited and had made fortunes out of the knowledge discovered by the devotees of these sciences, and to employ those funds in development on their own particular lines. He was astonished to learn that the Chemical Society had a Research Fund that produced only £220 a year. When they heard of the large fortunes made by the application of chemistry, he felt that one reason why they did not get more was some want of organisation to enable the societies to secure a very much larger proportion of the wealth gained from the increase of scientific knowledge. In the future he thought they should try to make one large scientific society, something like a guild, or ancient college, or brotherhood, which would hold property for the benefit of a great cause. He ventured to say that would be a much better way to advance science than by gifts of money to mixed corporations, such as universities. He had no faith in universities as promoters of scientific knowledge. Judging from the use made of the funds of the University of Oxford, no one could say that it was desirable to entrust any large sum of money, at the present moment, at any rate, to that University for the promotion of scientific research. The same would apply to the University of London. But societies, such as he suggested, could apply such funds without any danger of their being perverted to secondary uses.

Prof. Henry E. Armstrong proposed the toast of "Education." Speaking of the Universities, he said a head and centre was absolutely necessary for classical activity, but they could not but feel that

it was the duty of the Universities to exact from their sons also some understanding of science. Some knowledge of experimental phenomena should be aimed at in all culture.

Mr. T. H. WARREN responded first. He said that chemistry at Oxford was not what it ought to be, but its position was far different from that which it occupied some years ago. The universities were reviving the traditions of olden times. At Oxford there was a great school of chemistry and there were many young chemists there who would be heard of before long.

Sir ARTHUR W. RÜCKER next responded. He said it was the duty of a University to teach and to add to knowledge, and he confessed to receiving a shock at what Prof. Ray Lankester had said. He stoutly defended the University of London, and added that after all education was growing and we need not despair of English education.

Sir JOHN WOLFE BARRY also responded. He said he looked forward to great results from the Colleges at South Kensington. Speaking as an engineer, he thought his profession might be stated to rest upon chemistry, which taught them the composition and properties of materials. Civil engineers were deeply indebted to the Chemical Society.

Prof. THOMAS EDWARD THORPE proposed "The Guests."

Dr. EMIL FISCHER and Prof. J. A. EWING responded.

Thursday, April 18th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. W. S. Anderson and L. R. Scammel were formally admitted Fellows of the Society.

It was announced that the Council had appointed the following Committees for 1907—1908.

Finance Committee.—E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee.—W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee.—E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (*Chairman*), J. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee.—H. E. Armstrong, E. C. C. Baly, W. R, Dunstan, R. Meldola, G. T. Morgan, W. A. Tilden, J. Wade, and the Officers.

Research Fund Committee.—G. T. Beilby, W. R. Dunstan, P. F. Frankland, A. D. Hall, G. Matthey, R. Messel, H. Müller, Sir A. Pedler, W. H. Perkin, W. A. Tilden, and the Officers.

Certificates were read for the first time in favour of Messrs. :

Hugh Hague Copping, B.A., Cabourne, Caistor, Lincolnshire.
Matthewman Dalton Cowap, 21, Alma Square, St. John's Wood, N.W.
Eugen Fischer, Ph.D., Biebrich am Rhein, Germany.
Walter George Gledhill, M.A., Dersingham, Greenroyde, Halifax.
John Atkinson Jennings, 61, Gleneagle Road, Streatham, S.W.
Percival George Lloyd, 15, Woodside Road, Kingston-on-Thames.
Harold Pochin, B.A., 12, Chapel Street, Berkhampstead, Herts.
Charles Kenneth Tinkler, B.Sc., 297, Franklin Road, Kings Norton, Nr. Birmingham.

A certificate has been authorised by the Council for presentation for ballot under Bye-law I (par. 3) in favour of Mr. Thomas Kirkman Dealy, Craigmin East, Magazine Gap, Hongkong.

Of the following papers, those marked * were read :

***76. "The magnetic rotation of hexatriene, $CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, and its relationship to benzene and other aromatic compounds, also its refractive power." By Sir William Henry Perkin.**

In a paper on the magnetic rotatory power of aromatic compounds (*Trans.*, 1896, **69**, 1025) the very high rotations they possess have been pointed out ; the cause of this has been supposed to be due in the case of benzene to its ring formation, because the rotation of that substance is much higher than that of its isomeride dipropargyl.

This, however, became doubtful when it was found that *d*-$\Delta^{3:8(9)}$-*p*-menthadiene, which contains two unsaturated groupings in conjunction, gave abnormally high rotations, indicating the possibility that in benzene and other substances containing unsaturated groups in conjunction, the high rotations were also due to this circumstance. It was therefore desirable to examine some chain compound containing unsaturated groups in conjunction, in which there could be no influence due to ring formation. This was rendered possible by the examination of hexatriene, which contains three consecutive unsaturated groups.

Hexatriene was found to have a remarkably high rotation of 12·196. The difference in the formation of hexatriene and benzene is simply the difference of ring formation, due to the loss of 2 atoms of hydrogen. This affects the magnetic rotation by 0·982 and if that amount is subtracted from the above a value is obtained for the

magnetic rotation of benzene, based on the assumption that benzene contains three unsaturated groupings; this amounts to 11·214.

This number is practically that actually found for benzene, 11·284, and appears to point to two conclusions, namely, that benzene contains three contiguous unsaturated groupings (Kekulé's formula), and secondly that these have substantially the same values as in open chain compounds.

It is also noticed that the values of these unsaturated groups when in conjunction considerably increase with their number.

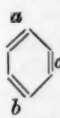
The refractive and dispersive power of hexatriene is very high, but the numbers do not show such a close relationship to benzene as do the magnetic rotations.

Discussion.

Mr. S. S. Pickles stated that the results obtained by Sir W. Perkin were of interest particularly to terpene chemists, who were frequently coming in contact with phenomena connected with systems of conjugated ethylenic linkings. The anomalous behaviour of compounds containing such an arrangement of double bonds called for some explanation. The fact that such compounds as phellandrene, $\Delta^{3:8(9)}$-*p*-menthadiene, and $\Delta^{1:3}$-dihydrobenzene, all of which contain the grouping ·C:C·C:C·, combine with only two atoms of bromine additively, instead of with four as might be expected, and the persistence of the remaining condition of unsaturation had often led chemists to wonder what was the state of affairs in conjugated ethylenic linkings. Sir W. Perkin's determinations had shown that from a physical standpoint there were reasons for assuming a somewhat similar condition to that prevailing in the benzene ring, and the speaker considered that the above-mentioned behaviour was to some extent chemical evidence in the same direction.

Thus, accepting certain properties and behaviour as the outcome of this arrangement of double bonds, the Kekulé formula becomes applicable and explanatory in the case of benzene.

Mr. Baly pointed out that in the Kekulé benzene formula



, the conjugation of double linkings is greater than in hexatriene; in benzene this effect occurs between the double linkings *a* and *b*, between *b* and *c*, and between *c* and *a*, whilst in hexatriene, $CH_2\overset{a}{:}CH\cdot CH\overset{b}{:}CH\cdot CH\overset{c}{:}CH_2$, the effect only occurs between *a* and *b* and between *b* and *c*, and not between *c* and *a*. He asked whether this increased conjugation might not be the origin of the fact that the magnetic rotation of benzene is higher than that of hexatriene by

0·07. He did not agree with Professor Armstrong's remarks that Sir William Perkin's results do not fit in with the modern views of the benzene molecule. The three double linkings as required by the Kekulé formula give rise to a definite amount of conjugation between them, and hence to a definite magnetic rotation. If the ring be flexible and in a state of pulsation or vibration, the total amount of conjugation would remain the same, as no energy leaves or enters the system. The magnetic rotation would therefore be the same as that demanded by the three static double linkings.

The PRESIDENT remarked that the fact that Sir W. Perkin had found results which proved that the Kekulé formula for benzene is the "true" one might be interpreted as implying that the Kekulé formula is the mean of the various possible formulæ for benzene, configurations which it undoubtedly assumes during its changes.

Sir W. H. PERKIN, in reply, said that it was well to bear in mind that the difference in rotation between the chain compounds hexatriene and hexane was practically the same as that existing between the ring compounds benzene and hexamethylene. That the two classes of compounds should possess different chemical properties did not seem surprising.

The difference of 0·07 between the rotation of benzene estimated from hexatriene and the found value was small and might partly be due to experimental error; it had therefore not been thought advisable to give any special significance to it in the meantime.

***77. "Aromatic azoïmides. Part I. *p*-Hydroxyphenylazoimide." By Martin Onslow Forster and Hans Eduard Fierz.**

The properties of camphorylazoimide have led the authors to investigate those of aromatic hydroxy-derivatives containing the N_3-nucleus in order to ascertain whether the behaviour of the first-named substance is not best explained by the constitutional formula $C_8H_{14}\begin{cases}C\cdot N_3\\ \|\\ C\cdot OH\end{cases}$.

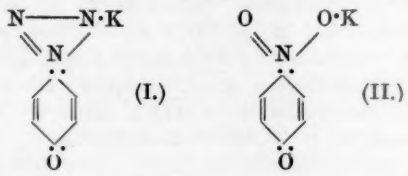
p-Hydroxyphenylazoimide, $HO\cdot C_6H_4\cdot N_3$, prepared by the action of hydroxylamine on diazotised *p*-aminophenol, is a colourless oil which has not been solidified, as an attempt to purify it by distillation under 1 mm. resulted in an explosion at 150°. The *benzoyl* derivative melts at 80°, and the *potassium* derivative has been obtained in two forms, coloured and colourless. The m-*nitrobenzoyl* derivative is faintly yellow and melts at 118°.

Nitrous acid converts *p*-hydroxyphenylazoimide into 3-*nitro*-4-*hydroxyphenylazoimide*, $C_6H_4O_3N_4$, a volatile, orange-coloured compound melting at 91°; the *benzoyl* derivative is colourless and melts at 103°.

Discussion.

Prof. Meldola asked whether the identity of the benzoyl derivatives prepared, on the one hand, by benzoylating the azoimide obtained by the author's method, and, on the other, from *p*-nitrophenyl benzoate by reduction, diazotisation, and conversion into the azoimide by the usual method, did not indicate that the compound possessed the phenolic as distinguished from the quinonoid constitution.

Dr. Morgan enquired whether the authors recognised any analogy between the isomeric potassium derivatives of their *p*-hydroxyazoimide and the two series of ethers obtained by Hantzsch and his collaborators from the nitrophenols. If such a comparison were valid the alternative formula I for the coloured potassium salt:



would indicate clearly the relationship existing between this salt and the coloured ether (formula II) of *p*-nitrophenol.

In reply to Professor Meldola, Dr. Forster stated that the benzoyl derivative of *p*-hydroxyphenylazoimide obtained from *p*-nitrophenol was slightly coloured, as indeed were most of the specimens obtained from the colourless potassium derivative of the azoimide compound, but the appearance of such specimens was quite distinct from that of the benzoyl derivative obtained from the blue salt of *p*-hydroxyphenylazoimide. He regarded Dr. Morgan's suggestion as an acceptable one, and stated that the bearing of Hantzsch's work upon the problem had been appreciated in the paper.

***78. "Measurements of the velocities of saponification of the *l*-menthyl and *l*-bornyl esters of the stereoisomeric mandelic acids." By Alexander McKenzie and Herbert Bryan Thompson.**

The authors find that *l*-bornyl *d*-mandelate is saponified more quickly than is *l*-bornyl *l*-mandelate. The esters were prepared from *d*- and *l*-mandelic acids respectively, and their velocities of saponification measured in ethyl-alcoholic solution under varying conditions of concentration and temperature.

l-Menthyl *d*-mandelate and *l*-menthyl *l*-mandelate (*Trans.*, 1904, 85,

1249) were also examined from the same standpoint; it was found that the former ester is the more readily saponifiable of the two.

A comparison of the velocities of saponification of the bornyl and menthyl esters shows that the former are much more quickly saponified than the latter (compare also *Trans.*, 1904, **85**, 378; 1905, **87**, 1004).

***79. "The constituents of the essential oil of American pennyroyal. Occurrence of a dextro-menthone." By Marmaduke Barrowcliff.**

The oil used in this investigation possessed the following characters: $d15°/15° = 0{\cdot}9297$; $a_D^{22} + 25°44'$ in a 1-dcm. tube; soluble in twice its volume of 70 per cent. alcohol. It has been found to consist of: (1) an undetermined phenol, in very small amount; (2) *l*-pinene (nitrosochloride, m. p. 103—104°; nitrolbenzylamine, m. p. 122°); (3) *l*-limonene (tetrabromide, m. p. 104°); (4) dipentene (tetrabromide, m. p. 124°), all of these terpenes being present in only small amount; (5) 1-methyl-3-*cyclo*hexanone (oxime, m. p. 41—43°; semicarbazone, m. p. 182—183°), about 8 per cent.; (6) pulegone (semicarbazone, m. p. 171°), about 30 per cent.; (7) *l*-menthone (oxime, m. p. 58—59°; semicarbazone, m. p. 184—186°), and (8) *d*-iso*menthone* (semicarbazone, m. p. 125—126°), identical with the dextrorotatory constituent of Beckmann's "inverted menthone"; the amount of these two menthones constituting about 50 per cent. of the oil; (9) a sesquiterpene alcohol, about 2 per cent.; (10) esters of formic, acetic, octoic, decylic, and salicylic acids, and the ester of a dibasic acid of the probable formula $C_8H_{14}O_4$, together with formic, butyric, octoic, and decylic acids in the free state; all these esters and acids being present only in small amount.

80. "Studies in the camphane series. Part XXIII. Oximes of camphorylsemicarbazide and camphorylazoimide." By Martin Onslow Forster and Hans Eduard Fierz.

The *oxime* of *camphorylsemicarbazide*, $C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\cdot CO\cdot NH_2\\ |\\ C:NOH\end{matrix}$, obtained from camphoryl-ψ-semicarbazide and hydroxylamine acetate, crystallises in lustrous, hexagonal plates, melts at 242°, and has $[\alpha]_D$ 105·4° in glacial acetic acid; an isomeric *oxime*, $C_{11}H_{20}O_2N_4$, produced by the action of cold dilute sulphuric acid on the foregoing substance, crystallises in lustrous needles, has $[\alpha]_D$ −37·7° in pyridine, and melts at 222°. The *benzylidene* compound, $C_{18}H_{24}O_2N_4$, the m-*nitrobenzylidene* compound, $C_{18}H_{23}O_4N_5$, and the *furfurylidene* compound, $C_{16}H_{22}O_3N_4$, melt at 205°, 215°, and 225° respectively.

The *oxime* of *camphorylazoimide*, $C_8H_{14}<\begin{matrix}CH\cdot N_3\\ C:NOH\end{matrix}$, melts at 84°, and, unlike camphorylazoimide itself, resists the action of cold alcoholic potash; on heating with this agent, hydrazoic acid is eliminated instead of nitrogen.

81. "The action of ethyl oxalate on thioacetanilide and its homologues." By Siegfried Ruhemann.

Homologues of dithioxanthoxalanil have been obtained by the action of sodium ethoxide and ethyl oxalate on the thioaceto-derivatives of *p*-toluidine, *m*-xylidine, and *β*-naphthylamine respectively. With caustic potash, they behave like dithioxanthoxalanil. The action of zinc dust and acetic acid on these compounds is unlike the behaviour of the reducing agent towards xanthoxalanil and its homologues which absorb six atoms of hydrogen (Ruhemann, *Trans.*, 1906, **89**, 1851) and yield colourless substances, whereas dithioxanthoxalanil is transformed into $C_{20}H_{16}O_3N_2$ (grey, shiny plates which decompose at about 240°). In this case, therefore, no addition of hydrogen takes place, but the whole of the sulphur is substituted by hydrogen; the following constitutional formula is therefore suggested for the compound: $PhN<\begin{matrix}CH_2\cdot CH & CO—CO\\ CO—C & CH\cdot CH_2\end{matrix}>NPh$. The substance, when digested with alkalis or alkali carbonates, yields blue salts of a red compound which has not yet been carefully examined, but is probably isomeric with the reduction product, $C_{20}H_{16}O_3N_2$, of dithioxanthoxalanil. This phenomenon resembles the transformation of the yellow product of the reaction between acetylacetone and phenylpropiolyl chloride into its red isomeride, which also yields blue salts (see Ruhemann and Merriman, *Trans.*, 1905, **87**, 1383).

82. "The action of tribromopropane on the sodium derivative of ethyl acetoacetate." By Thomas Edward Gardner and William Henry Perkin, jun.

When tribromopropane reacts with the sodium derivative of ethylacetoacetate the principal product is *ethyl γ-bromoallylacetoacetate*, $CH_2{:}CBr\cdot CH_2\cdot CH(COMe)CO_2Et$, which distils at 120° (8 mm.) and, when hydrolysed with alcoholic potash, yields *Δγ-butinene-α-carboxylic acid*, $CH{:}C\cdot CH_2\cdot CH_2\cdot CO_2H$ (m. p. 55—57°). Hydrolysis with dilute sulphuric acid converts ethyl γ-bromoallylacetoacetate into *γ-bromoallylacetone*, $CH_2{:}CBr\cdot CH_2\cdot CH_2\cdot COMe$, which distils at 83° (8 mm.), yields a liquid *oxime* and a crystalline *semicarbazone* (m. p. 150°), and

when reduced with sodium and alcohol is converted into *2-hydroxy-5-hexene* (methylcrotonylcarbinol),

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH(OH)Me.$$

Alcoholic potash hydrolyses γ-bromoallylacetone with elimination of hydrogen bromide and formation of *Δγ-butinene methyl ketone*,

$$CH{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}COMe.$$

This ketone distils at 149° (749 mm.), yields an *oxime* (m. p. 48°) and a *semicarbazone* (m. p. 136°), and gives a yellow precipitate of the copper derivative when its aqueous solution is mixed with ammoniacal cuprous chloride.

The sodium derivative of ethyl methylacetoacetate reacts readily with tribromopropane, and the *ethyl methyl-γ-bromoallylacetoacetate*, $CH_2{:}CBr{\cdot}CH_2{\cdot}CMe(COMe)CO_2Et$, thus produced, yields *Δδ-pentinene-β-carboxylic acid*, $CH{:}C{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2H$ (b. p. 207°), when it is hydrolysed with alcoholic potash.

Ethyl γγ-dibromodiallylacetoacetate, $(CH_2{:}CBr{\cdot}CH_2)_2C(COMe){\cdot}CO_2Et$, is produced in small quantity when tribromopropane is digested with the sodium derivative of ethyl acetoacetate. It is a viscid oil which distils at 175—180° (8 mm.), and is hydrolysed by alcoholic potash with formation of *Δαε-heptadi-inene-δ-carboxylic acid*,

$$(CH{:}C{\cdot}CH_2)_2CH{\cdot}CO_2H.$$

This acid melts at 48° and is converted by boiling with water into *m*-toluic acid (compare *Proc.*, 1906, **22**, 133).

83. "Indican. Preliminary notice." By Arthur George Perkin and William Popplewell Bloxam.

Indican, first described by Schunck (*Phil. Mag.*, [iv], **10**, 74, 1855, and *ibid.*, **15**, 122, 1858), has recently (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 520) been shown by Hoogewerff and Ter Meulen to be a well-defined, crystalline substance. As the result of experience gained by a study of the process of the latter chemists, the authors have devised a comparatively simple method for the isolation of this glucoside, by which a largely increased yield of the compound is obtained. The air-dried leaves of the *Indigofera Sumatrana* are extracted with acetone, the extract partially evaporated, and diluted with light petroleum which precipitates impure indican as a syrup; this after treatment with water is filtered, and the filtrate on concentration in a vacuum deposits the glucoside in a crystalline condition. The yield approximates to about 50 per cent. of that extracted by the acetone, although certain precautions are necessary. This process can be carried out entirely in the cold, and the contention of Schunck (*Chem. News*, 1900, **82**, 176) that his compound was distinct from the crystalline variety is thus evidently untenable. Experiments by Hoogewerff and Ter Meulen's

method (*a*) and the acetone process (*b*) have shown that the leaves of *Indigofera arrecta* also contain the same indican, but in this case the preparation is more troublesome owing partly to the presence of kaempferitrin (*Proc.*, 1906, **22**, 130), but more especially to that of a colourless, sugar-like compound, m. p. 186—187°, deposited in prisms from its alcoholic solution by means of ether. It resembles dulcite, but probably has the formula $C_6H_{12}O_5$ (found, C = 43·56 ; H = 7·44). Numerous air-dried preparations of indican melted at 57—58°, and samples obtained through the kindness of Prof. van Romburgh of Utrecht, and Prof. Beyerinck of Delft had also this property, so that the m. p. 51° of Hoogewerff and Ter Meulen may be a clerical error. When dried in a vacuum, indican fuses at about 100—101°, as stated by these chemists, but this appears to be due to the presence of water, for on further heating resolidification ensues, the product finally melting at 176—177°. Analysis of indican dried at 100° was in agreement with the formula $C_{14}H_{17}O_6N$ (H and t. M) (found, C = 56·83 ; H = 5·83), and when dried in a vacuum and allowed to regain a constant weight in moist air the figures approximated to $C_{14}H_{17}O_6N,2\frac{1}{2}H_2O$ (found, C = 49·89 ; H = 6·67 ; N = 4·38 ; H_2O = 13·80).

84. "Cupric nitrite." By Prafulla Chandra Ray.

A dilute solution of cupric nitrite slowly absorbs oxygen from the air and is converted into nitrate, following the law of mass-action. When a concentrated solution of cupric nitrite, however, is evaporated over sulphuric acid, even under diminished pressure, it partially decomposes according to the equation, $3Cu(NO_2)_2 = Cu(NO_3)_2 + 2CuO + 4NO$. The formula assigned to basic nitrite of copper by Hampe is untenable.

85. "The action of hydrogen peroxide on potassium cyanide." By Orme Masson.

The author finds that (1) hydrogen peroxide and potassium cyanide react exothermically in aqueous solution at the ordinary temperature.

(2) The peroxide is reduced without escape of oxygen so long as residual cyanide is present, but any excess of peroxide is afterwards decomposed into water and oxygen.

(3) The products of the oxidation of the cyanide, which do not include oxamide or oxalate, are potassium cyanate and potassium and ammonium carbonates. Cyanate is the primary product and tends to be converted by hydrolysis into carbonate through the catalytic agency of the peroxide.

(4) A part of the cyanide is converted by hydrolysis, without oxidation, into potassium formate and ammonia.

(5) The total oxidation product (cyanate plus carbonate) accounts for about four-fifths of the original cyanide, and the hydrolysis product (formate) for about one-fifth.

(6) The curve representing the progress of the reduction of peroxide, so long as unchanged cyanide remains, is of the second order and accords with the equation $\frac{dx}{dt} = k(A-x)\ (B-x)$, where A is the initial concentration of the peroxide, B that of the cyanide, and x the measure of the peroxide reduced, or cyanide oxidised, at time t. $B-x$ is the sum of the residual cyanide $(B-y)$ and its hydrolysed product (w).

(7) The hydrolysed product (w) reaches its maximum and final value ($W = 0{\cdot}2B$, nearly) before the completion of the oxidising action, and thereafter the slopes of the peroxide and cyanide curves are equal. The rate of hydrolysis is expressed by the empirical rule that $\frac{dw}{dt} = k_1(A-x)\ (W-w)$.

(8) If the solutions contain at the outset the ultimate products of the action itself, as well as fresh cyanide and peroxide, these products do not exert the influence indicated by the above equations. Hence some unknown intermediate condition probably occurs while the action is in progress.

(9) The addition of caustic potash or sulphuric acid at the outset greatly retards the whole action, but the addition of ammonia has very little effect.

86. "The reaction between calcium carbonate and chlorine water." By Arthur Richardson.

The author finds that cold chlorine water decomposes calcium carbonate with formation of calcium chloride and hypochlorous acid until 1 part of carbonate is dissolved in 30 parts of water, as shown by Williamson; $CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + 2HClO + CO_2$. At a later stage, calcium chloride, chlorate, and hypochlorite are formed, together with hypochlorous acid. This process goes on until from 40 to 50 per cent. of calcium chloride is obtained; beyond this point calcium carbonate is insoluble in chlorine water.

When chlorine water containing calcium carbonate in suspension is heated, oxygen is evolved and calcium chloride and chlorate are formed. In this case also, hypochlorous acid appears to be first produced, a part being then oxidised to calcium chlorate, another part reduced to

chloride, and a third part further reduced to free chlorine, whilst the hydrogen and part of the oxygen combine to form water, and the remainder of the oxygen is liberated.

87. "The density of hydrogen chloride." By Robert Whytlaw Gray.

Guye and Ter-Gazarian (*Compt. rend.*, 1906, **143**, 1233) have recently redetermined the density of this gas, and have calculated by means of it the physical atomic weight of chlorine. Some months ago the author made a series of weighings with the same object in view, but the results did not exhibit as good an agreement with each other as had been expected, and hence publication was deferred. At the request of Professor Guye, the results of the first series of measurements are now communicated. The gas was evolved by the action of pure concentrated sulphuric acid on pure solid sodium chloride in a vacuum, and was purified by fractional distillation at a low temperature. Six experiments were made. The highest value obtained for the weight of a litre of the gas at 0° and 760 mm. in London was 1·64091 grams, and the lowest 1·64026 grams. The mean value, corrected to lat. 45, is 1·6397 grams, which is practically identical with the value 1·6398 grams found by Prof. Guye.

88. "Di-iodocamphor." By James Ernest Marsh and Robert de Jersey Fleming Struthers.

In a former paper (*Trans.*, 1905, **87**, 1882), the authors stated that alkaline mercury cyanide did not form a derivative with camphor similar to that which it gives with certain other ketones. When, however, camphor is acted on by an alkaline solution of mercuric iodide containing potassium iodide, a *mercury* derivative of camphor is obtained. This substance is insoluble in water, but soluble in alcohol, and when treated with iodine gives mercuric iodide and *di-iodocamphor*. The latter substance forms brittle, yellow crystals melting at 108°, and soluble in alcohol, benzene, chloroform, or light petroleum. Its solution in chloroform is dextrorotatory. It is stable in the crystalline form, but its solution is decomposed by the action of light with separation of iodine.

89. "Acyl-ψ-derivatives of iminothiolcarbamic acid and their isomerides." By Augustus Edward Dixon and John Taylor.

The authors have made a further study of the additive compounds produced from acylogens and thioureas, and of the migration of acyl

groups within the resultant molecules (Dixon and Hawthorne, *Trans.*, 1907, **91**, 122).

Ethyl chlorocarbonate unites with phenylthiourea, yielding the hydrochloride of a feeble *base*, $NH{:}C(NHPh)\cdot S\cdot CO_2Et$, carbethoxylic iminophenylthiolcarbamide (otherwise, carbethoxy-ψ-phenylthiourea), which gives a *picrate*. When liberated from its hydrochloride, the base rapidly undergoes intramolecular change, the carbethoxy-radicle exchanging places with the hydrogen of the phenylamino-group, and thus furnishing the isomeric *aa*-carbethoxyphenylthiocarbamide, $CO_2Et\cdot NPh\cdot CS\cdot NH_2$, m. p. 133°. The hydrochlorides from *o*- and *p*-tolylthioureas yield *aa*-homologues, melting at 150° and 149° respectively.

Aryl chlorocarbonates also unite with aryl-monosubstituted thioureas; the products, on withdrawal of the halogen acid, yielding *aa*-disubstituted thiocarbamides, for example, $CO_2Ph\cdot NPh\cdot CS\cdot NH_2$.

Toluoyl chloride unites with thiourea and with phenylthiourea; the hydrochloride, $NH{:}C(NHPh)\cdot S\cdot CO\cdot CH_2Ph,HCl$, m. p. 131°, gives on treatment with calcium carbonate and alcohol the compound,

$$CH_2Ph\cdot CO\cdot NPh\cdot CS\cdot NH_2,$$

m. p. 114° (corr.), isomeric with the base; when melted, it undergoes further intramolecular change into another isomeride,

$$CH_2Ph\cdot CO\cdot NH\cdot CS\cdot NHPh,$$

m. p. 110°.

Attempts to isolate *aa*-benzoylphenylthiocarbamide failed, owing to the readiness with which the *ab*-form is produced. Palmityl chloride unites with thiourea and with phenylthiourea; from the latter combination, by withdrawal of the combined hydrochloric acid, *aa*-palmitylphenylthiocarbamide may be obtained.

Phenylbenzylcarbamic chloride, $CH_2Ph\cdot NPh\cdot COCl$, does not appear to yield a hydrochloride with phenylthiourea, the mixture, when warmed, decomposing with formation of benzylaniline and evolution of carbonyl sulphide.

Every *aa*-disubstituted monoacyl thiocarbamide so far examined gives thiocyanic acid when treated with strong caustic alkali; the supposed bases, $NH{:}C(NHPh)\cdot S\cdot CO_2Me$, &c. (Dixon, *Trans.*, 1903, **83**, 550), respond to this test, and hence must be regarded as *aa*-thiocarbamides.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Abegg, *Richard.* The electrolytic dissociation theory. Authorised translation by *Carl L. von* **Ende**. pp. vii + 180. New York. (*Recd.* 12/4/7.) From the Publishers: Messrs John Wiley and Sons.

American Electrochemical Society. Transactions. Vol. X. Philadelphia 1906. (*Reference.*) From Dr. F. Mollwo Perkin.

Berthelot, *Marcellin.* Traité pratique de l'analyse des gaz. pp. ix + 483. ill. Paris 1906. (*Recd.* 13/4/7.) From the Author.

Clowes, *Frank*, and **Coleman**, *J. Bernard.* Elementary practical chemistry. Part I. General chemistry. Part II. Analytical chemistry. Fifth edition. 2 vols. pp. xv + 198, xvi + 237. ill. London 1907. (*Recd.* 9/4/7.)

From the Publishers: Messrs. J. & A. Churchill.

Danneel, *Heinrich.* Electrochemistry. I. Theoretical electrochemistry and its physico-chemical foundations. Translated from the Sammlung Göschen by *Edmund S.* **Merriam**. pp. vii + 181. ill. New York 1907. (*Recd.* 12/4/7.)

From the Publishers: Messrs. John Wiley and Sons.

Meldola, *Raphael*, **Green**, *Arthur George*, and **Cain**, *John Cannell* [Editors]. Jubilee of the discovery of mauve and of the foundation of the coal tar colour industry by Sir W. H. Perkin. pp. 77. ill. London [1907]. (*Recd.* 21/3/07.) From the Executive Committee.

Whipple, *George C.* The value of pure water. pp. viii + 84. New York 1907. (*Recd.* 12/4/7.)

From the Publishers: Messrs. John Wiley and Sons.

II. *By Purchase.*

Eckel, *Edwin C.* Cements, limes, and plasters. Their materials, manufacture, and properties. pp. xxxiv + 712. ill. New York 1905. (*Recd.* 3/4/7.)

Paracelsus, *Theophrastus.* [Paracelsus his Archidoxis: comprised in ten books, disclosing the genuine way of making Quintessences, Arcanums, Magisteries, Elixirs, &c. . . . And finally his seven books, of the degrees and compositions of receipts, and natural things. Faithfully Englished, and Published by *J. H.* **Oxon**, London 1661.] pp. [vi] + 158 + [ii] + 176 [wrongly numbered 171]. Title-page missing. (*Reference.*)

III. *Pamphlets.*

Day, *Arthur L.* Mineral solution and fusion under high temperatures and pressures. (From the *Fifth Yearbook of the Carnegie Institution, Washington.*) 1907.

Gowland, *William.* Copper and its alloys in prehistoric times. (From the *J. Anthropological Inst.*, **36**, 1906.)

Lauder, *Alexander.* Variation in the composition of milk. pp. 52. Edinburgh 1906.

Richards, *Theodore William*, and **Behr**, *Gustavus Edward.* The electromotive force of iron under varying conditions, and the effect of occluded hydrogen. *Carnegie Institution of Washington, Publication* No. 61. 1906.

Richards, *Theodore William*, and **Forbes**, *George Shannon.* Energy changes involved in the dilution of zinc and cadmium amalgams. *Carnegie Institution of Washington, Publication* No. 56. 1906.

White, *Walter P.* The constancy of thermo-elements. (From the *Physical Review*, **23**, 1906.)

At the next Ordinary Meeting on **Thursday**, May **2nd**, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated:

"The chemical action of exradio. Part I. Action on distilled water." By Sir W. Ramsay.

"Freezing-point curves of the menthyl mandelates." By A. Findlay and E. M. Hickmans.

"The constitution of homo-eriodictyol. A crystalline substance from eriodictyon leaves." By F. B. Power and F. Tutin.

"The relation between valency and heats of combustion. Preliminary note." By G. Le Bas.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, May 2nd, 1907.

Allan, John Campbell,

91, Norse Road, Scotstoun, Glasgow.

Analytical Chemist. For 10 years assistant in the private Laboratory of Messrs. R. R. Tatlock & Thomson, Analytical and Consulting Chemists, Glasgow, and for 2 years was chief assistant. During the last 2 years was Chemist to the Cawnpore Sugar Works, Ltd., Cawnpore.

R. R. Tatlock. Harry Dunlop.
R. T. Thomson. John Clark.

James McLeod.

Bailey, Francis James,

Findon Hill, Sacriston, Durham.

Teacher. Inter. B.Sc. London University. At present Lecturer under the Durham County Council in Theoretical and Practical Inorganic Chemistry, and Student in the Sunderland Technical College with a view to taking Chemistry (Honours) in B.Sc. Exam. (London). Formerly Student at Barrow, and Royal College of Science, and Teacher of Chemistry in Organised School of Science, Bruce Grove, N.

W. Meredith. A. Crabtree.
A. Houldershaw. A. R. Gower.

Richd. Spencer.

Ball, William Robert,

48, Cambridge Road, Thornaby-on-Tees.

Science Teacher. A Chemistry Teacher at Secondary School, Stockton-on-Tees (1896—1907). B.Sc. (London) in Chemistry, &c.

J. G. Taylor. J. Seabury Smythe.
J. Handby Ball. *H. M. Atkinson.*

Walter Thorp.

Caldwell, Kenneth Somerville,

Demonstrator in Chemistry, St. Bartholomew's Hospital, E.C.

1851 Exhibitioner; Graduate of the Univ. of Wales (B.Sc., 1st Class Hons.), and of Leipzig (Ph.D., Summa cum Laude).

Kennedy J. P. Orton. James J. Dobbie.
W. H. Hurtley. Alexander Lauder.
H. W. M. Willett.

Cameron, Alexander Thomas,
Burtonhill, Malmesbury, Wilts.

Research Student in Chemistry. M.A., B.Sc. (Edin.), 1851 Exhibition Scholar (Edin., 1906), Assistant to the Lecturer in Chemistry, Surgeons' Hall, and Dick Veterinary College, Edinburgh, 1904—6. Author of: (i) "Variations in the Crystallisation of Potassium Hydrogen Succinate," *Proc. R.S.E.*, 25, 401—403; (ii) "Constitution of Complex Salts. I. Derivatives of the Sesquioxides," *Proc. R.S.E.*, 25, 722—737.

Hugh Marshall. Alex. Crum Brown.
Leonard Dobbin. William Ramsay.
Samuel Smiles.

Cunningham, John Arthur, B.A., R.U.I. & Cantab., A.R.C.Sc.I., Formerly 1851 Exhibition Research Scholar, Cambridge,
The Observatory, Alipore, Calcutta.

Professor of Chemistry, Presidency College, Calcutta. Author of "A Contribution to the Theory of the Order of Crystallisation of Minerals in Igneous Rocks," *Proc. Roy. Dublin Soc.*, IX., p. 383, 1901; "On an Attempt to Detect the Ionisation of Solutions by the Action of Light and Röntgen Rays," *Proc. Camb. Phil. Soc.*, XI., p. 431, 1902; "The Discharge of Electricity through Gases and the Temperature of the Electrodes," *Phil. Mag.*, Dec., 1902; "The Cathode Fall from Hot Carbon," *Phil. Mag.*, Feb., 1905, &c.

W. N. Hartley. W. E. Adeney.
P. C. Rây. Richard J. Moss.
James H. Pollok. S. Ruhemann.
Hugh Ramage.

Duckworth, Samuel, B.Sc.,
78, Alexandra Road, Lowestoft, Suffolk.

Lecturer in Science and Secondary School Teacher. Graduated B.Sc. (Victoria) and obtained M.Sc. in Chemistry. Lecturer in Chemistry in the Lowestoft Technical School.

Harold B. Dixon. G. H. Bailey.
D. L. Chapman. Norman Smith.
W. H. Perkin, jnr. J. F. Thorpe.

Fox, John Jacob,

6, Alkham Road, Stamford Hill, N.

Analyst in Government Laboratory. Royal College of Science, 1897–99; Government Laboratory since 1899; East London College since 1899.

T. E. Thorpe. H. W. Davis.
E. Grant Hooper. J. T. Hewitt.
C. Smith.

Gibson, Charles Stanley, B.A.,

45, Shakespeare Street, Manchester.

Engaged in research work at the Municipal School of Technology, Manchester. Second class Final Honour, School of Natural Science (Chemistry), Oxford University, 1905. Formerly, Natural Science Scholar of Corpus Christi College, Oxford.

W. J. Pope. W. W. Fisher.
John Watts. J. E. Marsh.
Henry A. Miers. D. H. Nagel.
S. J. Peachey.

Gregory, Joshua Craven,

126, Woodlands Road, Glasgow.

Analytical and Consulting Chemist and Metallurgist. B.Sc. (Lond.), F.I.C. Author of "A Short Introduction to the Theory of Electrolytic Dissociation" (Longmans, 1905), and "First Steps in Quantitative Analysis" (Edward Arnold, 1905). Joint author with F. W. Richardson, Esq., F.I.C., &c., of "Tartaric Acids and Tartrates, their Polarimetric Estimation," *J.S.C.I.* Analytical experience in the laboratories of F. W. Richardson, Esq. (Bradford City Analyst), and of T. V. Hughes, Esq., Birmingham; also at Kidderminster School of Science. At present partner in Robertson and Gregory, 128, Wellington Street, Glasgow, analysts. Also had experience in teaching chemistry at Kidderminster School of Science, &c.

F. W. Richardson. A. Jaffé.
Frederick D. S. Robertson. T. Vaughan Hughes.
J. B. Cohen.

Hall, Joseph Henry,

84, The Grove, Wandsworth, S.W.

Schoolmaster. Student in Chemical Laboratories for 8 years. Bachelor of Science, London University. Board of Education Certificates in Theor. Chemistry, Stages 2 and 3 Inorg., Stage 2

Organic; Prac. Chem., Stage 2, and Part I. Hons. Inorg., Stage 3 Organic.

Alfred Greeves. Frank E. Weston.
H. R. Ellis. W. G. Sewell.
H. Stanley Redgrove.

Harrington, Arthur George,
"Rochford," Westbury Road, Ealing, W.

Chemist. Major examination of the Pharmaceutical Society. Intermediate Examination of the Institute of Chemistry, and at present working under Mr. E. W. Lucas, F.I.C., F.C.S.

William Ramsay. Edward C. Cyril Baly.
Samuel Smiles. R. W. Gray.
N. T. M. Wilsmore. E. W. Lucas.
Arthur W. Crossley.

Harvey, Thomas Featherstone,
84, Henry Road, West Bridgford, Nottingham.

Analytical Chemist. Pharmaceutical Chemist (by examinations). Author of the following and other papers: "The Wijs Method of Determining the Iodine Value of Oils and Fats" (*Journ. Soc. Chem. Ind.*, 1902, 1437); "Determination of the Iodine Absorption of Oil of Turpentine" (*J.S.C.I.*, 1904, 413); "Detection and Estimation of Arsenic by the Gutzeit Test" (*Chemist and Druggist*, 1905, I. 168); "Temperature Corrections for Use with the Abbe Refractometer, &c." *J.S.C.I.*, 1905, 717); "The Composition of Nux Vomica Fat" (Harvey and Wilkie, *J.S.C.I.*, 1905, 718). Analyst and Works Chemist to manufacturing firms for the past 12 years.

R. M. Caven. Harold B. Holthouse.
Charles Spackman. *F. Stanley Kipping.*
L. Archbutt. *Peter MacEwan.*

Hope, Geoffrey Dodleston,
Heath Heys, Oxton, Birkenhead.

Student, working at present under Prof. Donnan at Liverpool University. B.Sc. (Victoria and Liverpool); Ph.D. (Halle, Germany).

J. Campbell Brown. F. G. Donnan.
A. W. Titherley. *W. Collingwood Williams.*
Prosper H. Marsden.

Houghton, Edward,
Glenhyrst, 106, Saltergate, Chesterfield.

Analytical Chemist (Iron Works). Matriculated at London, 1898. Lancashire County Council Science Scholar, 1900; 3 years' Metallurgical Training at Manchester School of Technology; 4 years'

experience as Assistant Works Chemist to the Darwen and Mostyn Iron Co., Darwen; 2 years' experience as Head Chemist to the Sheepbridge Coal and Iron Co., Chesterfield. Author of paper on the "Chemistry of Cast Iron," British Foundrymen Assoc., 1906. Reason for desiring admission, to keep in touch with pure science and other branches of applied science than my own.

Joseph West. Robert H. Pickard.
James Smith. *John Hanley.*
Samuel Banner.

Hubbard, The Hon. Raymond Egerton,
Addington Manor, Winslow, Bucks.
Undergraduate of Magdalen College, Oxford.

Harold Hartley. D. H. Nagel.
T. S. Moore. A. F. Walden.
N. V. Sidgwick.

Humphries, Herbert Brooke Perren,
117, Avenell Road, Highbury, N.

Science Master, Enfield Grammar School. B.Sc. (Hons. Chem.); A.R.C.Sc. (Chem.). Science Master, Enfield Grammar School. Engaged in research under the guidance of Dr. McKenzie at the Birkbeck College.

William A. Tilden. J. C. Philip.
M. C. Forster. Alex. McKenzie.
G. T. Morgan. Henry Wren.

Lewis, Carl,
P.O. Box 36, Johannesburg.

Chemist. Chemist and Druggist. Member of the Pharmaceutical Society of Great Britain. Practised Pharmacy for four years in Johannesburg. Studied for one year at the London College of Pharmacy, where I was medallist in Pharmacy.

George Gordon Watt. Thomas Tyrer.
Frederick W. Evans. *David J. Williams.*
Herbert A. Mills.

McConnan, James,
Danehurst, Greenbank Drive, Liverpool.

Assistant Lecturer and Demonstrator in Organic Chemistry, University of Liverpool. Degrees: M.Sc., Victoria and Liverpool; Ph.D., Jena. Publications: "Beiträge zur Kenntniss der Pyrazole" (Dissertation, Jena, 1904); "Labile isomerism among Acyl Derivatives

of Salicylamide" (in conjunction with Dr. A. W. Titherley), *Trans.*, 1906, **89**, 1318.

J. Campbell Brown. Prosper H. Marsden.
A. W. Titherley. F. G. Donnan.
W. Collingwood Williams.

Mitchell, Herbert Victor,
26, Brookfield Avenue, Walthamstow.

Analytical and Research Chemist. One time analyst and research chemist to Messrs. Burgoyne, Burbidges & Co.; two and a half years in Sir Boverton Redwood's Laboratory, and subsequently Assistant Demonstrator at East London College. Author, or part-author, of several papers published by the Society.

J. T. Hewitt. Boverton Redwood.
C. Smith. A. E. Dunstan.
T. W. Firth Clark.

Rhodes, Percy Joseph,
Bridge House, Church, Lancashire.

Technical Chemist, Bleacher, Dyer, and Calico Printer. Studied at the Macclesfield School of Science, Mechanics Institute, Stockport, and the Stockport Technical School. At present Technical and Works Manager for Messrs. F. Steiner & Co., Ltd., Turkey Red Dyers, Bleachers, and Calico Printers, Church Works.

Alfred J. King. William Marshall.
W. H. Pennington. L. G. Radcliffe.
Christr. Rawson. *J. C. Cain.*
A. G. Green.

Rixon, Frederic William, M.Sc., Ph.D.,
Powderham Road, Newton Abbot, Devonshire.

County Science Instructor. Assistant Professor of Chemistry, Merchant Venturers' College, Bristol. B.Sc. with 1st Class Honours in Chemistry, Victoria University. Fellow of the University. Ph.D., Giessen. Joint author of following papers: "On the Specific Heats of Carbon Dioxide at High Temperatures" (Brit. Assoc.) with Prof. H. B. Dixon; "Ueber die Kathodische Ausscheidung von Blei" (*Zeitsch. Elektrochem.*) with Prof. Elbs.

Harold B. Dixon. G. H. Bailey.
W. H. Perkin, jnr. Norman Smith.
J. F. Thorpe.

Robinson, John,
Agricultural College, Aspatria, Cumberland.

Analyst, and Lecturer in Chemistry (Agric. and Pure). National

Diploma in Agric., and National Diploma in Dairying. Advanced Certificates (Science and Art) in Pure and Agric. Chemistry. Three years a Student at the Agric. College, Preston. Now Lecturer (and Analyst) in Agric. and Pure Chemistry at Agric. College, Aspatria, Cumberland.

R. R. Swann. R. Henry Jones.
T. W. Fagan. *S. Hoare Collins.*

John Alexander.

Smith, Sydney William,
76, Norroy Road, Putney, S.W.

Assistant Assayer at the Royal Mint. Bachelor of Science (London). Associate of the Royal School of Mines. 1899—1902, Assistant to the late Sir William Roberts-Austen. 1902—1907, Assistant Assayer at the Royal Mint.

T. K. Rose. John Phelps.
W. Gowland. J. Brierley.
W. H. Merrett. F. W. Harbord.
E. O. Courtman. *G. T. Morgan.*

Sturrock, George Colleymore,
Aruvankad, Nilgiris, India.

Captain, Royal Artillery. Assistant Superintendent, Indian Cordite Factory. Studied at Royal Military Academy, Woolwich (2 years), and at Ordnance College, Woolwich (1 year) under Professor Hodgkinson.

W. R. Hodgkinson. William Rintoul.
Robert Robertson. Arthur H. Coote.

J. S. S. Brame.

Sutcliffe, Sam Mortimer,
4, Clive Place, Bradford.

Analytical Chemist. Partner in the firm of Sutcliffe and Murgatroyd, Analytical and Consulting Chemists. Assistant to C. Rawson, Esq., F.I.C. (Analytical Consulting Chemist), for two and a half years. Chief assistant for four and a half years to Messrs. Rawson and Petraczek. Formerly student in the Chemistry and Dyeing Department at the Bradford Technical College.

C. Rawson. *Joshua Knowles.*
Ad. Liebmann. *William E. Kay.*
Thorp Whitaker. *W. H. Pennington.*

William. G. White.

Tarr, Nicholas,

Lucton School, Herefordshire.

Lecturer in Science and Mathematics. One year student at University Tutorial College, London; 4 years student at St. George's Hospital, London; 4 years and 3 months Senior Master in Science and Maths. Passed Intermediate Exam. in Chemistry, Physics, and Zoology.

J. Addyman Gardner. Frank B. Last.
Chas. Slater. *F. G. Martin.*

Edmund Lamb.

Tebb, William Scott,

Sandfield, Putney Heath Lane, S.W.

Public Analyst for Southwark. M.A., M.D. (Cantab.), D.P.H., F.I.C.

Alexander Scott. W. D. Halliburton.
James Dewar. O. Rosenheim.

John M. Thomson.

Tonner, William Griffiths,

26, Gordon Road, Kingston-on-Thames.

Schoolmaster. B.Sc. (Univ. of Wales); Research Student at Birkbeck College, London; and Science Master at Tiffins' School, Kingston.

Alex. McKenzie. Claude M. Thompson.
Henry Wren. E. P. Perman.

Maurice Blood.

The following Certificate has been authorised for pre-entation to Ballot by the Council under Bye-law I (3):

Dealy, Thomas Kirkman,

Craigmin East, Magazine Gap, Hongkong.

Second Master, Queen's College, Hongkong (Hongkong Civil Service). As a Student in Training, passed the South Kensington Advanced Course of Inorganic Chemistry, and went through a year's laboratory practice in Inorganic Chemical Analysis (Qualitative), metals and non-metals. Take a lively interest in Chemical Science, both as student and practical teacher.

T. Luxton.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

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PROCEEDINGS

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CHEMICAL SOCIETY.

Vol. 23. No. 325.

Thursday, May 2nd, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Mr. A. V. Hussey was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs.:

Owen Aubrey Elias, 123, Waller Road, New Cross, S.E.
Walter Harold Nuttall, 55, Market Street, Watford, Herts.
Walter Ormston Young, Springfield, Cartmel, Lancs.
Israel Hyman Zortman, B.Sc., Sternwartenstr. 44 II r, Leipzig.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

John Campbell Allan.
Francis James Bailey.
William Robert Ball, B.Sc.
Kenneth Somerville Caldwell, B.Sc., Ph.D.
Alexander Thomas Cameron, M.A., B.Sc.
John Arthur Cunningham, B.A.
Thomas Kirkman Dealy.
Samuel Duckworth, B.Sc.
John Jacob Fox.
Charles Stanley Gibson, B.A.
Joshua Craven Gregory, B.Sc.
Joseph Henry Hall, B.Sc.
Arthur George Harrington.
Thomas Featherstone Harvey.
Geoffrey Doddleston Hope, B.Sc., Ph.D.
Edward Houghton.
Hon. Raymond Egerton Hubbard.
Herbert Brooke Perren Humphries, B.Sc.
Carl Lewis.
James McConnan, M.Sc., Ph.D.
Herbert Victor Mitchell.
Percy Joseph Rhodes.
Frederic William Rixon, M.Sc., Ph.D.
John Robinson.
Sydney William Smith, B.Sc.
George Colleymore Sturrock, Capt. R.A.
Sam Mortimer Sutcliffe.
Nicholas Tarr.
William Scott Tebb, M.A., M.D.
William Griffiths Tonner, B.Sc.

Of the following papers, those marked * were read:

***90. "The chemical action of the radium emanation. Part I. Action on distilled water." By Sir William Ramsay, K.C.B.**

A qualitative confirmation of the fact noticed by Rutherford that the emanation from radium, in decaying, evolves a large amount of heat has been obtained; the relative amounts of hydrogen and oxygen produced by the action of radium bromide on water, amounting to 32 c.c. of explosive gases per gram of radium per one hundred hours, have been measured, and also the excess of hydrogen, of which the mean value is 5·5 per cent., reckoned on the total gas. Reasons were adduced to show that hydrogen is not one of the products of degradation of radium, and other hypotheses to account for the excess of hydrogen were considered.

The action of the emanation alone on water also decomposes it into explosive gas, mixed with excess of hydrogen; it has been shown that the emanation, when mixed with explosive gas, causes recombination, and the rate at which the decomposition of water takes place has been measured.

The reason of the production of excess of hydrogen has not yet been elucidated.

Discussion.

Professor Tilden said that although the subject which had been brought before them by the President would probably not admit of much discussion, they would be ready to unite in expressing their admiration of the remarkable skill which had been displayed in the manipulation and measurement of such strange material in quantities so minute. They must also commend the self-restraint which Sir William Ramsay had imposed on himself in refraining from speculation in a field which offered so much temptation and where there was room for so much difference of opinion.

The President, in answer to a question, replied that the emanation was an inactive gas, in the sense of not forming compounds, but at the same time, a most active gas, inasmuch as it decomposes or disintegrates into a series of other bodies, some of which, at least, are capable of chemical combination.

***91. "Freezing point curves of the menthyl mandelates." By Alexander Findlay and Evelyn Marion Hickmans.**

From a study of the freezing point curve for mixtures of *l*-menthyl *l*-mandelate and *l*-menthyl *d*-mandelate, it is found that *l*-menthyl

r-mandelate exists as a definite, partially racemic compound having a stable melting point of 83·7°. By applying the law of mass action and the law of the depression of the freezing point by dissolved substances, the degree of dissociation of the partially racemic compound has been calculated to be about 50 per cent. It was also pointed out that other freezing point curves indicate the existence of true racemates in the liquid state.

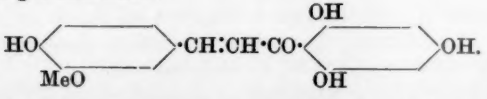
Discussion.

The President asked whether it had been proved that racemic compounds possessed double the molecular weight of the *d*- or *l*-compounds, and whether they might therefore be regarded as composed of one molecule of each variety.

Dr. Findlay, replying to Dr. Lowry, stated that calculations had not been made with regard to the stability of hydrated salts, but that the method of calculation referred to would be applicable also in such cases. In reply to the President, Dr. Findlay stated that the arguments adduced for the existence of a racemic compound held only for the fused state, not for solutions, although it is highly probable that undissociated racemic compounds exist to some extent even in solution.

***92. "The constitution of homo-eriodictyol. A crystalline substance from eriodictyon leaves." By Frederick Belding Power and Frank Tutin.**

The substance designated *homo-eriodictyol*, $C_{16}H_{14}O_6$ (m. p. 223°), previously isolated and described by the authors (*Pharm. J.*, 1906, **77**, 381, and *Abstr.*, 1906, **90**, ii, 885), has now been further investigated. It is isomeric with hesperitin (*Ber.*, 1881, **14**, 970), and similar to the latter in many of its properties, but its sodium compound has the normal formula $C_{16}H_{13}O_6Na$ (compare Perkin, *Trans.*, 1898, **73**, 1037). Homo-eriodictyol contains one methoxyl group and yields a *tetra-acetyl* derivative, $C_{16}H_{10}O_6(COMe)_4$ (m. p. 154°). On fusion with potash it gives protocatechuic acid. When homo-eriodictyol is hydrolysed with a concentrated aqueous solution of potassium hydroxide it yields phloroglucinol and ferulic acid (4-hydroxy-3-methoxycinnamic acid). From these results it is concluded that homo-eriodictyol must possess the following constitution:



The "eriodyctionon," recently described by Mossler (*Annalen*, 1907, **351**, 233), is evidently identical with homo-eriodictyol.

Eriodictyol, $C_{15}H_{12}O_6$ (m. p. 267°), a crystalline substance which was also isolated by the authors from eriodictyon leaves (*loc. cit.*), contains no methoxyl group. When heated with acetic anhydride it yielded two compounds, melting at 137° and 195—196° respectively. It is considered probable that homo-eriodictyol is a mono-methyl ether of eriodictyol.

93. "The relation between valency and heats of combustion. Preliminary note." By Gervaise Le Bas.

It is now known that valency is a volume property of the atoms (Barlow and Pope, *Trans.*, 1906, **89**, 1675; Le Bas, *Trans.*, 1907, **91**, 312), and the author has found that valency may also be regarded as an energy property; this conclusion can be illustrated with the aid of the heats of combustion of the hydrocarbons.

The heat of combustion of a substance may be regarded as made up of (*a*) an absorption of heat due to the dissociation or decomposition and (*b*) an evolution of heat due to the combination of the isolated atoms with oxygen. A study of molecular heats of combustion, however, reveals the following law, which appears to be generally valid. *The heat of combustion of an organic compound is equal to the sum of the heats of combustion of its possible dissociation products.*

The conclusion is therefore drawn that the factor *a* is negligibly small as compared with *b*. In illustration of this may be cited the facts that the heats of combustion of a normal paraffin and its carboxyl derivatives are identical provided that the physical state be taken into account, and that the heats of combustion of associated substances or of polymerides are the same as those of an equivalent number of simple molecules. It may be shown that the thermal constants of the alcohols, ethers, organic halogen compounds, carboxylic acids, esters, nitriles, amines, mercaptans, and other classes of compounds also follow this law.

The heats of combustion of organic compounds in most cases are found to be the same as those of saturated and unsaturated hydrocarbons and hydrogen, or of mixtures of these. Similarly, the factor *a* is negligibly small as compared with *b* in the case of the saturated and unsaturated hydrocarbons, and therefore their heats of combustion are sensibly those of their isolated atoms, *plus* an excess for the latter, owing to unsaturation. The additive relations obtained lead to a second law which applies to all the hydrocarbons.

The molecular heats of combustion of the hydrocarbons are proportional to their valency numbers W. For example, the heat of combustion of a

normal paraffin, C_nH_{2n+2}, in the gaseous state is given by the expression

$$M.H.C. = (6n+2)c = W.c.,$$

c being a constant, representing the heat equivalent of one hydrogen atom expressed in large calories.

This law is illustrated by the following table, in which Thomsen's values are used:

		W.	c.	$W.c$.	Calc. $M.H.C$.
Methane	CH_4	8	26·49	211·7	211·9
Ethane	C_2H_6	14	26·45	370·4	370·4
Propane.....	C_3H_8	20	26·46	529·2	529·2
Butane	C_4H_{10}	26	26·43	687·9	687·2
Pentane.....	C_5H_{10}	32	26·46	846·7	847·0
Mean			26·46		

The heat value of the difference for the homologous increment CH_2 is calculated to be equal to $6c = 6 \times 26{\cdot}46 = 158{\cdot}76$, which is similar to that observed.

The conclusion is also drawn that the molecular heats of combustion of compounds do not lend themselves to the determination of constitution. From certain peculiarities which are connected with olefine and acetylene linkings, it is, however, possible to recognise the presence of the latter in a compound with certainty.

94. "The velocity of hydrolysis of aliphatic amides by alkali."
By James Codrington Crocker and Frank Harold Lowe.

The rate of reaction of the aliphatic amides with sodium hydroxide has been investigated at from 40·06° to 95·9°.

The reactions are shown to follow the bimolecular relation

$$K = \frac{1}{at}\left[\frac{1}{c} - \frac{1}{c^\circ}\right],$$

where a is the degree of dissociation of the alkali. The graphs between the reciprocal of concentration and time are very approximately straight lines with a slight curvature indicating a small retarding effect of the neutral salt. If the amides are arranged in decreasing order of reactivity, this order is: formamide, acetamide, propionamide, capronamide, butyramide, *iso*butyramide, valeramide, the temperature variation of reactivity over the above range is best expressed by the formula $\log K = \log K^\circ + B\left(\frac{1}{T^\circ} - \frac{1}{T}\right) + C\left(\frac{1}{T^\circ} - \frac{1}{T}\right)^2$.

The mean differential coefficient of the graph between $\log K$ and $\frac{1}{T}$ for the above range is less than for the analogous case of hydrolysis by acid. The view is taken that hydrolysis by alkali of the amides proceeds by the direct action of the hydroxyl ion on the amide

molecule. A modification of the Arrhenius hypothesis was suggested to explain the exponential variation of reactivity with temperature, a parallel being drawn between tautomeric change, where difference of property is produced by the "wandering" of an atom, and "electromeric" change, where difference of property is caused by the movement of an electron.

95. "The addition of iodine to acetylenic acids." By Thomas Campbell James and John Joseph Sudborough.

Good yields of the di-iodides of tetrolic and phenylpropiolic acids are formed when a concentrated aqueous solution of cupric sulphate (1 mol.) is gradually run into a well-stirred aqueous solution of the potassium salt of the acid (1 mol.) mixed with an excess of potassium iodide. The di-iodides may be isolated by warming the solution, removing the cuprous iodide, and acidifying with a mineral acid.

The same di-iodides may be prepared by mixing aqueous solutions of the potassium salts with an excess of a potassium solution of iodine in iodide and allowing to stand for several days.

Definite di-iodides could not be isolated from *o*- and *p*-nitrophenylpropiolic acids, or from acetylenedicarboxylic acid, although in the two former cases an addition of iodine occurs.

Olefinic acids, even when they contain conjugated bonds, do not combine with iodine to any appreciable extent.

The velocity constants for the reactions between a solution of iodine in potassium iodide and the potassium salts of tetrolic, phenylpropiolic, *o*- and *p*-nitrophenylpropiolic acids have been determined. The reaction in each case is bimolecular when aqueous solutions are employed.

The reaction between iodine and phenylpropiolic acid has been studied in absolute alcoholic and in aqueous alcoholic solutions, both with and without the addition of potassium iodide.

96. "The chemical changes induced in gases submitted to the action of ultra-violet light." By David Leonard Chapman, Samuel Chadwick, and John Edwin Ramsbottom.

An apparatus specially designed for the examination of the chemical changes brought about in gases by the influence of the light emitted from a mercury lamp was described. With the aid of the apparatus the conversion of oxygen into ozone, the interaction of carbon monoxide and oxygen, and the decomposition of carbon dioxide have been investigated particularly with a view to ascertaining the effect, in each case, of the presence of varying amounts of water vapour.

Dry carbon dioxide is decomposed by ultra-violet light, the percentage decomposition being increased by a reduction of pressure, but, under the same conditions, the moist gas at all pressures remains practically unchanged. The rate of contraction of a mixture of carbon monoxide and oxygen is practically independent of the degree of desiccation of the gases, and this was found to be due to the fact that, although the presence of moisture causes the rate of formation of carbon dioxide to rise, it results in a equivalent reduction in the yield of ozone.

97. "Studies of the perhalogen salts. Part. I." By Charles Kenneth Tinkler.

The well-known formation of periodides by the addition of iodine to a solution of an iodide has been investigated by means of the ultra-violet absorption spectra of the solutions. Whilst neither a *N*/100 aqueous solution of iodine nor dilute solutions of iodides show any characteristic absorption in the ultra-violet, the aqueous solutions of iodine, after the addition of various iodides, all give the same spectra, which show a large amount of general absorption and two absorption bands.

Solutions of iodine to which various soluble bromides or chlorides have been added also give evidence, from their spectra, of the presence of addition compounds of the halogen salt and iodine.

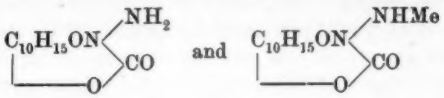
It can be shown from the spectra of the solutions, that with equimolecular quantities of potassium iodide, bromide or chloride combination takes place most readily with the iodide and least with the chloride. On the addition of hydriodic, hydrobromic, or hydrochloric acids to the aqueous solution of iodine, the spectra of the solutions are the same as those containing the corresponding metallic salts; hydriodic acid, however, appears to combine with iodine when the acids are passed into a chloroform solution of this substance.

98. "The interaction of cyanodihydrocarvone, amyl nitrite, and sodium ethoxide." By Arthur Lapworth and Elkan Wechsler.

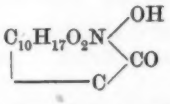
Cyanodihydrocarvone, when subjected to the action of amyl nitrite and sodium ethoxide, is converted into a compound, isomeric with the expected *iso*nitroso-derivative, but which investigation has shown to be a *lactam*, $C_{10}H_{14}ON<\begin{smallmatrix}NH\\|\\C\end{smallmatrix}$; this is feebly acidic and may be converted into a neutral *methyl* derivative, $C_{10}H_{14}ON<\begin{smallmatrix}NMe\\|\\CO\end{smallmatrix}$. On treatment with

dilute alkali these yield the corresponding *amino-acids*, from which they may again be obtained by means of dihydrating agents.

The lactams are converted by cold acids into *lactonic bases*,



which, on hydrolysis with hot dilute acids, yield ammonia and methyl amine respectively, together with a *lactonic acid*,



which, although it may be titrated in the cold as a monobasic acid, is probably not carboxylic in character; with warm alkalis the lactone ring is severed and the compound behaves as a dibasic acid.

All these compounds, by prolonged treatment with hot mineral acid, are converted into a pseudo*cumene carboxylic acid* ($CO_2H : Me_3$ = probably 1 : 2 : 3 : 5). This is dimorphous, the forms melting at 84° and 105—106 respectively.

99. "Contributions on the chemistry of oxygen compounds. II. The compounds of cineol, diphenyloxide, nitroso-derivatives, and the carbamides with acids and salts." By Robert Howson Pickard and Joseph Kenyon.

The authors have investigated the capacity of various compounds containing oxygen to form additive compounds analogous to those of the phosphine oxides (Part I., *Proc.*, 1906, **22**, 42) with the view of throwing some light on the influence (if any) of the phosphorus atom. No regularity can be observed in the molecular proportion of substances containing oxygen in their additive compounds.

It is suggested that the formation of additive compounds by sulphoxides and nitroso-compounds and the non-formation of the same, in general, by sulphones, nitro- and azoxy-compounds is probably due to the position of the oxygen atoms of the latter in a ring, so that any subsidiary or residual valency is internally satisfied. As the aryl substituted carbamides form salts and as, in general, the carbamides behave in regard to the formation of additive compounds in a similar manner to the phosphine oxides, cineol &c., it is probable that the additive compounds formed by the carbamides are due to the subsidiary valency of the oxygen atom, which in these compounds, as in the

phosphine oxides, is influenced by the proximity of the nitrogen or phosphorus atom respectively. The additive compounds of cineol with magnesium alkyl halides are decomposed when heated, and the product when treated with dilute acids yields Δ^1-*p*-terpineol (8).

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Saturday, 8th June, 1907.

Those Fellows who received grants in June, 1906, or whose grants, allotted in June of previous years, have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Saturday, 1st June, next.

On Thursday, June 13th, 1907, Professor J. B. Farmer, F.R.S., will deliver a discourse entitled "Some Borderline Problems in Botany."

ERRATUM.

1907. P. 120, line 16 from top, *for* "Toluoyl" *read* "Phenylacetyl."

At the next Ordinary Meeting, on Thursday, May 16th, 1907, at 8.30 p.m., the following papers will be read:

"The relation between the crystalline form and the chemical constitution of simple inorganic substances." By W. Barlow and W. J. Pope.

"Experimental investigation into the process of dyeing." By J. Hübner.

"Some derivatives of *p*-pyranol allied to certain derivatives of brazilein and hæmatein." Preliminary communication. By W. H. Perkin, jun., and R. Robinson.

"Mixed semi-ortho oxalic compounds." By G. D. Lander.

"The mechanism of bromination of acylamino-compounds." Preliminary notice. By J. B. Cohen and W. E. Cross.

"Separation of cadmium from zinc as sulphide in the presence of trichloracetic acid." By J. J. Fox.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 30/5/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 326.

Thursday, May 16th, 1907, at 8.30 p.m., Prof. R. MELDOLA, F.R.S., Past President, in the Chair.

Mr. E. Gardner was formally admitted a Fellow of the Society.

It was announced that the following address would be presented to the Société Chimique de France on the occasion of the celebration of its Jubilee.

ADDRESS FROM THE CHEMICAL SOCIETY TO THE SOCIÉTÉ CHIMIQUE DE FRANCE.

The ties of sympathy connecting the Chemical Society of France and the Chemical Society resemble the bonds uniting members of the same family rather than those associating friends drawn together by mere community of interests.

On the occasion of our Jubilee celebration in 1891 your representative, M. Gautier, then President of the Société Chimique de Paris, reminded us that, prior to your foundation in 1857, M. Wurtz had paid a special visit to London in order to study the organisation of our Society, which had then been in existence for sixteen years, and further remarked "La Société Chimique de Londres a été le modèle et la grande sœur de la Société Chimique de Paris."

It is now the privilege of the elder sister to send through her appointed delegates the congratulations of all English chemists to the Société Chimique de France on completing fifty years of active work in

widening the boundaries of a science which has conferred such inestimable benefits on humanity.

How magnificent have been the contributions to knowledge made by your Society during those five decades is witnessed by your Bulletin, which in itself represents a historical survey of modern chemistry.

The satisfaction with which our Society embraces this opportunity of taking part in your réunion is not untinged by sadness, for we can no longer hope to meet amongst you two of the most illustrious of our confrères, whose loss your country, and indeed the whole world, have so recently had to deplore. This loss is felt all the more deeply by us since one of them was the doyen of our Honorary and Foreign Fellows.

In the genius of Marcellin Berthelot, the gifted founder of chemical synthesis and of thermochemistry, were united the savant and the statesman, a combination of qualities which must be rare in any age; whilst in Henri Moissan we mourn a colleague, the products of whose industry have been well described as taking a place amongst the greatest achievements in inorganic chemistry.

(Signed) WILLIAM RAMSAY, *President.*
ALEXANDER SCOTT, *Treasurer.*
M. O. FORSTER, } *Honorary*
ARTHUR W. CROSSLEY, } *Secretaries.*
HORACE T. BROWN, *Foreign Secretary.*

Certificates were read for the first time in favour of Messrs.:

William Arthur Colebourn, 34, Camp St., Broughton, Manchester.
Robert Cornthwaite, Agricultural Laboratory, Halifax.
Charles William Lamb Jensen, Oakhill, Nr. Bath.
Charles Horne Warner, 24, Gordon Street, Gordon Square, W.C.

A certificate has been authorised by the Council under Bye-Law I (par. 3) in favour of Ruchi Ram Sahni, M.A., Government College, Lahore, India.

Of the following papers, those marked * were read:

***100. "The relation between the crystalline form and the chemical constitution of simple inorganic substances." By William Barlow and William Jackson Pope.**

The authors pointed out that only two simple homogeneous close-packed assemblages of equal spheres exist; one of these possesses holohedral cubic symmetry, and the other holohedral hexagonal sym-

metry with the axial ratio, $a:c=1:0{\cdot}8165$. They showed that close-packed homogeneous assemblages made up of two or more kinds of spheres of nearly the same size must approximate in marshalling to one or other of the above types of assemblage or some homogeneous combination of these. All the known crystalline forms exhibited by the elements can be interpreted in the light of the above geometrical principles; the latter also explain how binary compounds composed of two elements of the same valency, such as the alkali halogen compounds, crystallise in the cubic system and how silver iodide, which crystallises in the hexagonal system, exhibits the axial ratio, $a:c=1:0{\cdot}8196$.

An examination of the isomorphous series of tri-halogen compounds, to which the compounds CsI_3 and RbI_3 belong, shows that the axial ratios of these orthorhombic substances are also in accordance with the geometrical principles stated above.

Descriptions were given of the homogeneous assemblages corresponding to the above substances and to the ammonium salts isomorphously related to certain of them. The crystalline forms of certain of the chlorates, carbonates, and nitrates were also discussed.

Discussion.

Dr. Divers pointed out that, for the purposes of the authors, it was surely unnecessary and, as introducing complexity, undesirable to do more than equalise the axial ratios of similar crystals by applying the law of the rationality of the axes. When the authors went on to multiply the equalised ratios by the factor, $\sqrt[3]{W/ac}$, and entitled the results, "equivalence parameters," they served no useful end, since no further "equivalence" could be conferred upon ratios (or anything else, except their more complex expression) by multiplying them by this or any other factor.

He feared that the authors were risking failure to convince many chemists of the sufficiency of the assumption of their "valency volumes" to correlate chemical with crystalline structure, by demanding for the purpose of appropriate close packing that considerable deviations from simply proportioned volumes must be allowed them; for example, that volumes of a given valency are not quite equal, even under similar conditions, when they are of different chemical elements; and that, under different conditions, these volumes may vary considerably, even when of the same element; and that, also, for close packing along with preservation of mechanico-chemical structure, the valencies must be, sometimes, exceptionally chosen; that, for example the alkali metals are to be univalent in their trihalides; sulphur

bivalent in sulphates; nitrogen, tervalent in nitrates, and oxygen in hydroxyl compounds, sometimes of no valency.

What seemed to him to be, also, a serious objection to the packing of atoms to represent chemical constitution was that juxtaposition of atoms expressed chemical union in some cases and not in others. He also doubted whether with close packing and pressing out all interspaces the appropriate distances between the centres of the spheres, shown undeformed in the models and diagrams, would be sufficiently preserved. But, without the experience of the authors, that was too difficult a point for others to deal with adequately.

Dr. TUTTON said he was glad that Prof. Pope in his exposition of the authors' paper had removed the doubt which had been created by their first paper as to the light in which they regarded the use of topic axial ratios. It was now made clear that their equivalence parameters were intended to supplement, for unrelated or only morphotropically related substances, the teaching of topic axial ratios with respect to the strictly related members of isomorphous series, and that the value of topic axial ratios for expressing the structual relationships of the members of such series was undoubted by them. He pointed out that these ratios depended solely on constants determinable with the highest experimental accuracy, namely, the crystallographic axial ratios, the molecular weight, and the specific gravity, and that whilst the molecular volume represented the total relative change of volume on passing from one member to another, the topic axial ratios gave the actual changes in the separation of the structural units, the chemical molecules, in the three directions of space. The equivalence parameters of the authors suffered from an apparent want of such precision, essentially so from the different nature of the problem, and Dr. Divers had seized on this apparent weak point. He (Dr. Tutton) felt sure, however, having now had time to consider the previous paper of the authors and having seen the present one by their courtesy, that they would be able fully to justify their position, and that they were on the right track. He believed that the topic axial ratios and the equivalence parameters would together afford a complete account of the relationship between crystalline structure and chemical constitution, and it was pleasant to think that the papers introducing both had been communicated to this Society.

*101. "Experimental investigation into the process of dyeing." By Julius Hübner.

The author has examined quantitatively the absorption of basic, acid, and direct dyeing colouring matters by cotton, wool, silk, and

other fibrous materials at different temperatures, with and without the addition of other substances to the dye-bath.

Parallel series of measurements were made on the absorption of the several classes of colouring matters by charcoal, graphite, China clay, and lampblack, and the following conclusions were established from the comparison.

Fibres of animal origin behave towards colouring matters in the main like charcoal, whilst cotton behaves similarly to graphite.

Thus both cotton or graphite are practically unaffected by acid dye-stuffs, either hot or cold, whilst wool or charcoal absorb the colouring matter freely.

The parallel behaviour of cotton and graphite and of wool and charcoal is also illustrated by the effect of acids, sodium sulphate, &c., added to the dye-bath in the case of both acid and direct dyeing colouring matters. Similar analogies of behaviour are observed in the absorption of basic colours by the materials mentioned.

The relative absorptions were determined at different temperatures.

Discussion.

Dr. Divers pointed out the importance of this work as showing that dyeing was not of a chemical, but of a physical, nature. The fact that absorption by charcoal was of the same order of things as absorption of colours by fibres was of much interest.

Mr. Grant Hooper said that in the brief *résumé* of the paper which the author had given the conclusions had not been stated, and he asked whether the increased amount of colouring matter taken up by disintegrated cotton as compared with the unbroken fibre was not explained by the fact that the colour more easily gained access to the interior of the fibre when the latter was torn. He suggested that the imbricated structure of wool probably facilitated the access of dye substance to the interior of that fibre, and so accounted in a similar manner for the comparative readiness with which wool also took up colouring matter.

He further asked whether, in view of such apparent action and of the results obtained in the experiments with fibrous material on the one hand and charcoal and inorganic substances on the other, the conclusion was drawn that the dye was retained by a process of adsorption.

Dr. Feilmann remarked that Suida had also published extensive accounts of experiments on the dyeing of mineral substances, &c., some two years or more ago, and that Suida's results seemed to show that a kind of double decomposition occurred, so that the process was of a more or less chemical character, whereas Mr. Hübner's

experiments, on the other hand, tended rather to show that the process was mainly physical, depending on absorption.

102. "Esterification constants of substituted acrylic acids. Part II." By John Joseph Sudborough and Ebenezer Rees Thomas.

As an extension of the work already published (*Trans.*, 1905, **87**, 1840), the authors have determined the esterification constants of a number of unsaturated acids with methyl alcohol at 15°. The acids experimented with were cinnamic, phenyl*iso*crotonic, β-ethylacrylic, ethylidenepropionic, and allylacetic. The results indicate in a decisive manner the retarding effect which a double bond in the αβ-position has on the velocity of esterification. The constants for phenyl*iso*crotonic and cinnamic acid are in the ratio 74 : 1, and of the β-ethylacrylic, ethylidenepropionic, and allylacetic acids in the ratio 1 : 50 : 26·7.

103. "The addition of bromine to the α- and β-chloro- and bromocinnamic acids and their methyl esters." By John Joseph Sudborough and Gwilym Williams.

The products obtained by the addition of bromine to the α- and β-bromo- and chloro-cinnamic acids and their methyl esters have been examined in order to determine whether in each case the α- or β-compound and the stereoisomeric *allo*-compound yield the same dibromide.

The addition of bromine to the α-compounds does not take place readily in the dark. In daylight both α-bromo-acids yield the same *ααβ-tribromo-β-phenylpropionic acid*, m. p. 151—152°. The corresponding *methyl ester* melts at 47—48°. The two β-bromo-acids combine with bromine, both in the dark and in light, yielding the same *αββ-tribromo-β-phenylpropionic acid*, m. p. 146—147°. The corresponding *methyl ester* melts at 42—43° (decomp.). The α-chloro-acids do not combine with bromine in the dark, and in daylight each yields a mixture of two dibromides, which, so far, have not been separated.

The two β-chloro-acids combine more readily with bromine, yielding the same *β-chloro-αβ-dibromo-β-phenylpropionic acid*, m. p. 143—144° (decomp.).

104. "The addition of bromine to unsaturated compounds. Part I." By John Joseph Sudborough and John Thomas.

The work, of which a preliminary note has already appeared (*Proc.*, 1906, **22**, 318), has been continued. The rate of addition of bromine to various olefine acids has been determined at 15° in carbon tetrachloride solution. The accelerative effect of sunlight has been confirmed. Of the following acids examined, cinnamic, crotonic, phenyl-*iso*crotonic, undecylenic, oleic, elaidic, erucic, brassidic, β-ethylacrylic, ethylidenepropionic, and allylacetic acids, all those containing the double linking in the $\alpha\beta$-position unite with bromine but slowly in the dark, whereas all the other acids absorb bromine with great readiness under the same conditions, the reaction being practically complete in a few minutes.

The characteristic behaviour of the $\alpha\beta$-unsaturated acids may be used as the basis of a method for determining whether a double linking is in the $\alpha\beta$-position with respect to the carboxylic group or not.

105. "Separation of cadmium from zinc as sulphide in the presence of trichloroacetic acid." By John Jacob Fox.

A convenient method of separating cadmium from zinc as sulphide is furnished by the use of trichloroacetic acid. The quantity of trichloroacetic acid required is at least 10 grams per 100 c.c. of solution, but much greater concentrations can be used without affecting the precipitation of cadmium as sulphide. Even when the amount of the cadmium is small (5 milligrams per 100 c.c.), concentrations of trichloroacetic acid as great as 30 grams of acid per 100 c.c. do not prevent the whole of the cadmium being precipitated.

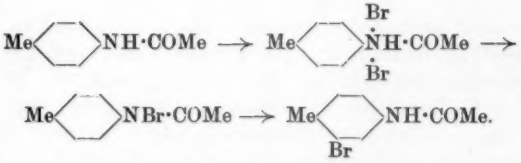
In this respect, trichloroacetic acid differs from both hydrochloric and sulphuric acids.

For the complete separation of cadmium and zinc, two precipitations are desirable; this is unnecessary, however, when the proportions of cadmium and zinc are about equal or when the cadmium is present in excess. If the presence of trichloroacetic acid is objectionable in the subsequent treatment of the solutions, a first partial separation of zinc and cadmium may be effected by the use of 1 gram of hydrogen chloride per 100 c.c. of solution.

106. "The mechanism of bromination of acylamino-compounds." Preliminary notice. By Julius Berend Cohen and William Ernest Cross.

In the ordinary process of brominating acylamino-compounds in acetic acid solution, the crystalline product which is first formed yields, on pouring it into water, the nuclear brominated compound. This intermediate compound has been isolated in the case of aceto-*p*-toluidide and crystallises in brilliant, yellow needles containing two atoms of bromine. It is very unstable in the dry state, slowly losing bromine and changing into the original compound. The same result is more rapidly effected by shaking the ethereal solution with mercury or dry potassium carbonate. The ether then contains the unchanged aceto-*p*-toluidide. If, on the other hand, the bromine compound is poured into water or shaken with pyridine, &c., hydrogen bromide is at once eliminated and a quantitative yield of 2-bromoaceto-*p*-toluidide is obtained.

The following provisional explanation is offered. An additive compound with one molecule of bromine is first formed, which in contact with water loses hydrogen bromide and gives the nitrogen bromide compound. The latter rapidly isomerises to the nuclear substituted product:



This view would conform to that of Chattaway and Orton (*Ber.*, 1899, **32**, 3576), in which the formation of the nitrogen bromide compound is found to precede the isomeric change from side-chain to nucleus. Up to the present, however, the authors have failed to obtain evidence of the presence of the nitrogen bromide compound.

107. "Mixed semi-ortho-oxalic compounds." By George Druce Lander.

The amide chlorides of methyl and ethyl oxanilates are stable below 100°. On decomposition by heat they pass by loss of hydrogen chloride into the imide chlorides, which are further resolved into alkyl chloride, carbon monoxide, and phenylcyanate, thus:

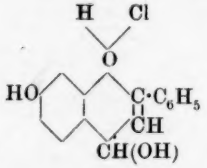
$$CO_2R\cdot CCl_2\cdot NHPh \longrightarrow CO_2R\cdot CCl{:}NPh + HCl \longrightarrow O{:}C{:}NPh + RCl + CO.$$

With sodium alkyloxides the amide chlorides yield *triethyl anilido-semi-ortho-oxalate*, $CO_2Et\cdot C(OEt)_2\cdot NHPh$, m. p. 69—70·5°, b. p. 172—174°/12 mm., and *trimethyl anilidosemi-ortho-oxalate*, similarly constituted, and having m. p. 80—82°, b. p. 182°/20 mm.

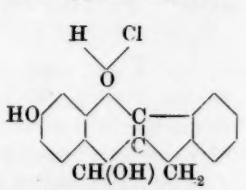
When heated under atmospheric pressure these compounds yield *ethyl* iso*diphenyloxaluric ethyl ester*, $PhN{:}C(OEt)\cdot NPh\cdot CO\cdot CO_2Et$, m. p. 101—104°, and the corresponding *methyl* iso-*ester*, m. p. 131—133° respectively. Both *iso*-esters on hydrolysis with hydrogen chloride give diphenylparabanic acid.

108. "Some derivatives of γ-pyranol allied to certain derivatives of brazilein and hæmatein." (Preliminary communication.) By William Henry Perkin, jun., and Robert Robinson.

o-Hydroxybenzaldehyde and its derivatives condense with certain acetophenone or hydrindone derivatives to form derivatives of γ-pyranol. Thus β-resorcylaldehyde and acetophenone condense readily when their solution in acetic acid is saturated with hydrogen chloride, and the 7-*hydroxy*-2-*phenyl*-1 : 4-*benzopyranol hydrochloride*,



thus produced, is identical with the substance prepared by Bülow and Sicherer (*Ber.*, 1901, **34**, 3890) from benzoylacetaldehyde by condensation with resorcinol. If the acetophenone is replaced by 1-hydrindone, 7-*hydro y*-2 : 3-*indeno*-1 : 4-*benzopyranol hydrochloride*,

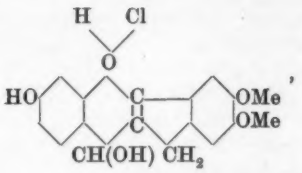


is produced. This substance crystallises with 2 molecules of water and yields, with platinum chloride, the double *salt*

$$(C_{16}H_{12}O_3,HCl)_2PtCl_4$$

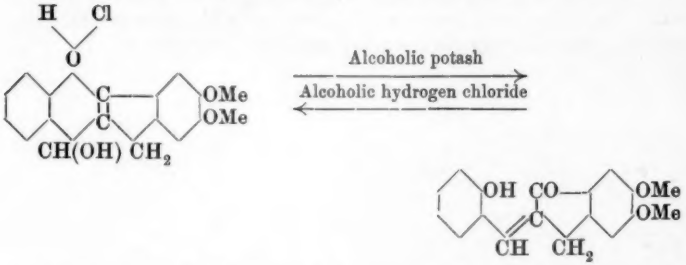
and, with gold chloride, the *salt* $C_{16}H_{12}O_3HCl,AuCl_3,H_2O$.

7-Hydroxy-5 : 6-dimethoxy-2 : 3-indeno-1 : 4-benzopyranol hydrochloride,



is obtained when β-resorcylaldehyde and 5 : 6-dimethoxy-1-hydrindone are condensed by hydrogen chloride in methyl-alcoholic solution. Similar condensations have also been carried out with salicylaldehyde and *p*-methoxysalicylaldehyde and 5 : 6-dimethoxyhydrindone.

The pyranol derivatives thus produced may also be obtained by the action of alcoholic hydrochloric acid on the corresponding *o*-hydroxybenzylidene-1-hydrindones and, conversely, the latter are again produced from the pyranols by the action of alcoholic potash. The following example will serve as an illustration of these important changes:



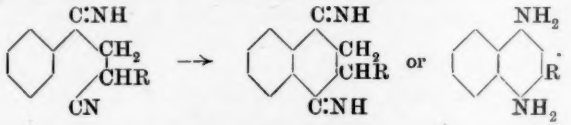
The authors wish to reserve, for a short time, the further investigation of the above and similar condensations.

109. "Arsenic di-iodide." By John Theodore Hewitt and Thomas Field Winmill.

The authors have prepared and analysed the arsenic di-iodide described by Bamberger and Philipp (*Ber.*, 1881, **14**, 2643). The molecular weight determined by the elevation of boiling point in carbon disulphide solution shows the compound to have the formula As_2I_4. The substance is, however, useless for the preparation of aromatic analogues of cacodyl, since the only product isolated from the action of magnesium phenyl bromide is triphenylarsine. Pyridine decomposes the compound immediately with liberation of arsenic.

110. "The formation and reactions of imino-compounds. Part IV. The formation of 1 : 4-naphthylenediamine from ethyl γ-imino-α-cyano-γ-phenylbutyrate." By Jocelyn Field Thorpe.

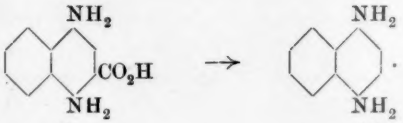
In continuation of the work already published in Parts II and III of this series it was shown that derivatives of benzene having a side-chain of three carbon atoms substituted at the α-carbon atom by a nitrile group and at the γ-carbon atom by an imino-group pass on treatment with cold concentrated sulphuric acid into derivatives of 1 : 4-naphthylenediamine, ring formation taking place between the ortho-hydrogen atom of the benzene ring in respect to the side-chain and the carbon atom of the nitrile group. The general formula for this reaction can therefore be represented as follows:



Ethyl γ-imino-α-cyano-γ-phenylbutyrate (1) passes on treatment with cold concentrated sulphuric acid into ethyl 1 : 4-naphthylenediamine-3-carboxylate (2):

(1). (2).

This ethyl salt yields 1 : 4-naphthylenediamine-3-carboxylic acid (3) on hydrolysis, from which 1 : 4-naphthylenediamine (4) can be prepared on heating at 200° in a current of hydrogen:



(3). (4).

111. "Mercury derivatives of pseudo-acids containing the group ·CO·NH·." By Samuel James Manson Auld.

Unlike cyanuric acid which forms two isomeric mercuric salts (Hantzsch, *Ber.*, 1902, **35**, 2717), all the pseudo-acids containing the group ·CO·NH· examined have given only one derivative, in all cases

an *N*-salt containing the group ·CO·Nhg·. Some of these *N*-mercury salts act as "mercury acids" and form alkali salts. Violuric acid, for instance, forms a series of coloured alkali mercuriviolurates, which can be obtained both in the hydrated and anhydrous states. The pseudo-acids examined include uric acid and its alkyl derivatives, ψ-uric acid, methyluracyl, violuric and dimethylvioluric acids, saccharin, benzoylcyanamide, and carbostyril.

112. "The influence of substitution in the nucleus on the rate of oxidation of the side-chain. III. Oxidation of the nitro- and chloronitro-derivatives of toluene." By Julius Berend Cohen and Henry James Hodsman.

The authors have studied the rate of oxidation of the nitro- and chloronitro-toluenes, the same method being employed as that previously described (*Trans.*, 1904, **85**, 174, 1622). Excluding the 4-chloro-2-nitrotoluene, which occupies an exceptional position in the series, the general result of the oxidation of the ten isomeric chloronitrotoluenes may be summarised as follows. The compounds with the nitro-group in the ortho-position are least oxidised, those with the nitro-group in the para-position are most oxidised, whilst the meta-compounds stand midway between the two. The same result is obtained with the three isomeric nitrotoluenes. The position occupied by 4-chloro-2-nitrotoluene appears to depend on the length of time during which the substance is in contact with the oxidising agent, the quantity of acid formed varying inversely with the time of oxidation. This has been explained by showing that in all the *o*-nitro-compounds the acid first formed undergoes further oxidation and that this is especially the case with the 4-chloro-2-nitro-compound. The result is that the quantity of acid as well as the total yield of products is low, in other words, the more protracted the oxidation, the more of the acid, first formed, is destroyed.

The authors also described the preparation of 3-chloro-2-nitrotoluene which was originally obtained by one of them in conjunction with H. G. Bennett, so that all the isomeric chloronitrotoluenes are now known.

113. "The reducibility of magnesia by carbon." Preliminary note. By Roland Edgar Slade.

Three distinct methods were attempted for establishing the reducibility of magnesia by carbon. The first consists in heating magnesia and carbon together in an enclosed furnace, with arc or resistance heating, and collecting and analysing the gaseous products

of reaction; considerable quantities of carbon monoxide and some carburised magnesium were in this way obtained.

The second method is an application of that employed by R. S. Hutton and J. E. Petavel (*Proc. Roy. Soc.*, 1907, A 79, 155) for investigating the reduction of alumina, and consists in employing a bath of molten electrolytic copper as a solvent and condenser for the metal vapour.

These experiments were carried out in carbon tube furnaces and in crucibles heated under the electric arc; alloys of copper and magnesium were obtained at temperatures as low as 1700°. In the carbon tubes the sublimed magnesia also reacts with the heated walls of the tubes, from which a powder containing carburised magnesium can be collected on cooling.

The third method has not up to the present proved successful, but consists in heating a mixture of magnesia and carbon to known temperatures in a current of nitrogen gas, the product being examined for nitride. The temperature of reduction of magnesia seems to be above the limit of temperature at which the nitride is stable.

The two methods which have furnished a positive result give independent confirmation of the recent experiments of Lebeau (*Compt. rend.*, 1907, **144**, 799). Whereas this author considers that the reduction only occurs at or above the boiling point of magnesia when the vapour of carbon and magnesia come in contact, the present research seems to show that the reaction can take place at temperatures below the melting point of this oxide.

114. "The reaction between organo-magnesium halides and nitro-compounds." Preliminary note. By Robert Howson Pickard and Joseph Kenyon.

Aromatic nitro-compounds react very vigorously with an organo-magnesium halide in ethereal solution.

p-Nitrotoluene thus forms an indefinite amorphous yellow *compound*, which, when treated with acids, yields principally *p*-nitrosotoluene, *p*-tolylhydroxylamine, *pp'*-azoxytoluene (probably by the interaction of the two former compounds), and *p*-toluidine.

The authors wish to reserve for a time the study of this new reaction.

115. "A method for the determination of the equilibrium in aqueous solutions of amines, pseudo-acids and bases, and lactones." By Tom Sidney Moore.

The compounds mentioned in the title resemble each other in that their aqueous solutions contain, in addition to ions, two non-ionised forms. The relations may be represented by the equations:

$$\text{For a pseudo-acid: } H\cdot X{:}O \overset{(1)}{\rightleftharpoons} X\cdot OH \overset{(2)}{\rightleftharpoons} XO' + H^{\cdot}$$

$$\text{For an amine: } NX_3 + H_2O \overset{(1)}{\rightleftharpoons} NX_3H\cdot OH \overset{(2)}{\rightleftharpoons} NX_3H^{\cdot} + OH'$$

The reaction constants of the reactions (1) and (2) cannot in general be determined directly, although their determination is a matter of considerable importance; for the constant of reaction (2) is the true ionisation constant of the acid or base; and the constant of reaction (1) represents the relation between the two forms of the pseudo-acid, or between the amine and its hydroxide as the case may be.

The author showed that these constants, as well as their temperature coefficients, may be calculated from the results of measurements of the partition of the substance between water and another solvent, and of the "apparent" ionisation constant (as calculated from the electrical conductivity, or from degree of hydrolysis of salts) at different temperatures.

116. "The 'true' ionisation constants, and the hydration constants of piperidine, ammonia, and triethylamine." By Tom Sidney Moore.

The equations developed in the preceding paper were applied to the results of the partition experiments of Hantzsch and Sebaldt, Hantzsch and Vagt, and of Dawson and McCrae, and the values of the true ionisation constants (k_1) and of the hydration constants (k_2) determined for different temperatures.

$$k_2 C_{NX_3} = C_{NX_3HOH}$$
$$\text{and } k_1 C_{NX_3HOH} = C^{NX_3H^{\cdot}} \times C_{OH'}.$$

At 20° the results were:

	$k_1 \times 100$.	k_2.
Piperidine	0·156	2·83
Ammonia.....	0·0052	0·56
Triethylamine	0·064	1·86

Further, the heat of neutralisation of the three bases and the heat of solution of ammonia were calculated and found to agree satisfactorily with the experimental values.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Alessandri, *P. E.* Merceologia tecnica. Vol. I. Materie prime greggie e semi-lavorate di uso commerciale ed industriale. Vol. II. Prodotti chimici inorganici ed organici. pp. xi + 530, xi + 515. ill. Milano 1907. (*Recd.* 9/5/7.) From the Publisher: Ulrico Hoepli.

Lister Institute of Preventive Medicine. Collected papers, No. 3. London 1906. (*Recd.* 15/5/7.) From the Director.

Matthews, *J. Merritt.* The textile fibres: their physical, microscopical, and chemical properties. 2nd edition. pp. viii + 480. ill. New York 1907. (*Recd.* 6/5/7.)
From the Publishers: Messrs. John Wiley and Sons.

National Physical Laboratory. Collected researches. Vol. II. pp. 310. ill. [London 1907.] (*Recd.* 1/5/7.) From the Director.

—— Report for the year 1906. pp. 61. ill. Teddington 1907. (*Recd.* 1/5/7.) From the Director.

Roth, *W. A.* Physikalisch-chemische Übungen. pp. xii + 174. ill. Hamburg 1907. (*Recd.* 25/4/7.)
From the Publisher: Leopold Voss.

Settimj, *Luigi.* Caoutchouc e gutta-percha. pp. xvi + 253. ill. Milano 1907. (*Recd.* 9/5/7.) From the Publisher: Ulrico Hoepli.

Sheppard, *S. E.*, and **Mees**, *C. E. Kenneth.* Investigations on the theory of the photographic process. pp. x + 342. ill. London 1907. (*Recd.* 10/5/7.) From the Authors.

Van Nostrand's Chemical Annual, 1907. A handbook of useful data. Edited by *John C.* **Olsen.** pp. x + 496. London 1907. (*Recd.* 6/5/7.)
From the Publishers: Messrs. A. Constable & Co.

Vogel, *Hermann Wilhelm.* Photochemie und Beschreibung der photographischen Chemikalien. Fünfte Auflage, bearbeitet von *Ernst* **König.** pp. xi + 376. ill. Berlin 1906. (*Recd.* 13/5/7.)
From the Publisher: Gustav Schmidt.

II. *By Purchase.*

Allen, *Alfred H.* Commercial organic analysis. 3rd. Edition. Vol. II. Part III. Acid derivatives of phenols, aromatic acids, resins, and essential oils. Revised by the Author and *Arnold Rowsby* **Tankard.** pp. xiii + 547. London 1907. (*Recd.* 22/4/7.)

Lassar-Cohn. Arbeitsmethoden für organisch-chemische Laboratorien. Spezieller Teil: Erste Hälfte. Vierte Auflage. pp. 864. Hamburg 1907. (*Recd.* 15/5/7.)

Wedekind, *Edgar.* Zur Stereochemie des fünfwertigen Stickstoffes. Zweite Auflage von *Emil* **Fröhlich.** pp. 93. Leipzig 1907. (*Recd.* 15/5/7.)

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Saturday, 8th June, 1907.

Those Fellows who received grants in June, 1906, or whose grants, allotted in June of previous years, have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Saturday, 1st June, next.

On Thursday, June 13th, 1907, Professor J. B. Farmer, F.R.S., will deliver a discourse entitled "Some Borderline Problems in Botany."

ERRATUM.

1907. P. 137, line 12 from top, *for* "$N/100$" *read* "$N/1000$."

At the next Ordinary Meeting, on **Thursday, June 6th, 1907, at 8.30** p.m., the following papers will be read:

"The relation between absorption spectra and chemical constitution. Part VII. Pyridine and some of its derivatives." By F. Baker and E. C. C. Baly.

"The interaction of methylene chloride and the sodium derivative of ethyl malonate." By F. Tutin.

"Molecular weight of β-naphthol in solution in solid naphthalene." By E. P. Perman and J. H. Davies.

"Synthesis of hexatriene derivatives." Preliminary notice. By I. Smedley.

"The constitution of the diazo-compounds." By J. C. Cain.

"*p*-Cresol sulphoxide and sulphide." By S. Smiles and T. P. Hilditch.

"*p*-Dioxyphenylsulphoxide." By S. Smiles and A. W. Bain.

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Issued 18/6/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 327.

Thursday, June 6th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. A. T. Cameron, G. Fowles, S. W. Smith, and J. W. Yates were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. :

Frank Buckney, B.A., 51, Highbury Park, N.
William Hay, Holton House, Beverley Road, Hull.
George Joseph Saunders, B.E., School of Mines, Charters Towers, Queensland, Australia.
David Willott, B.Sc., Rosedale, Thorncroft Road, Sutton, Surrey.
Hubert Arthur Wootton, B.A., B.Sc., 20, Great College Street, Westminster, S.W.

Of the following papers, those marked * were read :

***117. "The relation between absorption spectra and chemical constitution. Part. VII. Pyridine and some of its derivatives." By Frank Baker and Edward Charles Cyril Baly.**

The authors have made a spectroscopic examination of pyridine and its substitution products, with the object of determining the influence of the nitrogen atom and also the constitution of the pyridones. It was shown how the nitrogen atom tends to restrain the motions of the

ring, this restraint being very much lessened by the addition of acid to the solutions. A very similar effect is produced by the substitution by chlorine, inasmuch as the basicity of the nitrogen is thereby considerably reduced.

In the case of the oxypyridines, the α- and β-compounds were shown to be true pyridones, whilst the β-isomeride possesses the hydroxylic configuration.

***118. "The interaction of methylene chloride and the sodium derivative of ethyl malonate." By Frank Tutin.**

The reaction which takes place when methylene chloride is heated with an alcoholic solution of the sodium derivative of ethyl malonate has been studied, and the following three crystalline by-products resulting from the condensation were examined.

1. A sodium salt crystallising from alcohol in yellow leaflets.
2. An *acid* crystallising in needles, which melt at 132°.
3. An *acid* obtained in small needles, which are insoluble, or nearly so, in all solvents.

The yellow sodium salt was obtained by Perkin and Prentice (*Trans.*, 1891, **59**, 991), but was not further examined by them. It has the formula $C_{15}H_{21}O_8Na$, and yields a liquid *acid*, $C_{14}H_{21}O_6{\cdot}CO_2H$, which gives a violet coloration with ferric chloride. On hydrolysis, this acid first gives an *acid* melting at 305°, but, when completely hydrolysed, yields a *tetracarboxylic acid*, $C_6H_8(CO_2H)_4$ (m. p. 138—139°). The latter compound, although melting at the same temperature as *cis-cyclo*hexane-1 : 2 : 4 : 5-tetracarboxylic acid, is not identical with it.

The substance melting at 132° possesses the formula

$$C_{18}H_{24}O_6(CO_2H)_2,$$

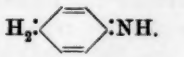
and, on hydrolysis, yields an *acid* melting at 306°.

The insoluble substance is hydrolysed by sodium carbonate, giving a *sodium* salt, $C_{32}H_{35}O_{20}Na_3,6H_2O$, crystallising in white needles; the corresponding *potassium* salt is insoluble and anhydrous. The *acid*, $C_{29}H_{25}O_{14}(CO_2H)_3$, obtained from these salts crystallises in leaflets melting at 200°.

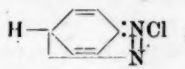
***119. "The constitution of the diazo-compounds." By John Cannell Cain.**

None of the formulæ hitherto proposed for the diazo-salts can account for the great ease with which such compounds lose their diazo-nitrogen. Nitrogen attached to the benzene ring, as, for example, in the case of aniline, is readily eliminated only by oxidation, and

Ostrogowich and Silbermann have recently shown that in this process aniline probably assumes the tautomeric form



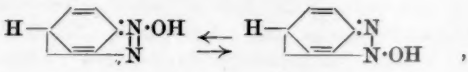
As the diazotisation process closely resembles this reaction the author proposed for diazobenzene salts (chloride) the quinonoid formula.



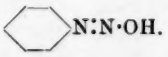
this bears much analogy to the formula of quinonechloroimide, which also loses nitrogen on boiling with water.

The new formula explains why, in compounds where the atom in the para-position to the amino-group is already saturated, no diazo-salt can be formed, thus, for example, *ac*-tetrahydronaphthylamine and 4-aminoquinoline yield no diazo-salts. For a similar reason no aliphatic diazo-chlorides are known.

The corresponding formula for the diazohydroxide may, unlike the chloride, give rise to two tautomeric forms :



the latter of which represents the constitution of the normal or *syn*-diazo-compounds and is closely related to the formula for the *iso*- or *anti*-compounds :



As these formulæ fully explain the reactions of the diazo-compounds the stereochemical theory is rendered unnecessary.

The following recommendations as to nomenclature were suggested.

(i) The word "diazonium" should be retained for the diazo-salts.

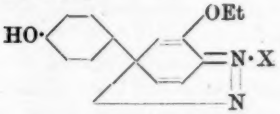
(ii) The normal or *syn*-metallic diazo-compounds should be called normal diazo-oxides or diazo-oxides.

(iii) The *iso*- or *anti*-compounds should be called *iso*-diazo-oxides.

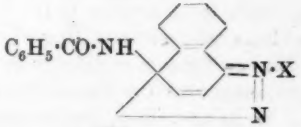
Discussion.

Dr. Morgan said that the retention of the quinquevalency of the salt forming nitrogen atom and the representation of the mobility of the diazo-group N_2 by means of the doubly linked attachment to the aromatic nucleus were both strong arguments in favour of the new formula for diazonium salts. It must, however, not be forgotten that

other types of diazo-derivatives, the diazoamines and the acyl-*p*-diazoimides, for example, also readily give up their diazo-nitrogen, and it still remained to be seen whether this formulation could be extended to those cases. The new formula represented diazonium salts as substances of a quinonoid type, but so long as the radicle in the para-position to the diazo-nitrogen was hydrogen or a simple saturated group (methyl, methoxyl, &c.) there was no development of colour; when, however, this hydrogen was replaced by a complex aromatic group then the compound exhibited colour. The stable yellow diazo-salts having the general formula I were a case in point (Cain, *Trans.*, 1905, **87**, 5).



(I.)



(II.)

Having been engaged for some time in the investigation of compounds of this nature he hoped, in conjunction with Mr. Wootton, to bring forward at the next meeting a complete series of coloured stable diazo-salts (formula II) derived from *p*-aminobenzo-*a*-naphthalide. A formula such as that advocated by Dr. Cain afforded a satisfactory explanation of the properties and reactions of these substances.

Dr. Hewitt drew attention to the coloured diazonium salts which had been obtained by different chemists. Some of the earliest to be isolated were those derived from *p*-semidine bases; these were not merely coloured, but Jacobson found that they were remarkably stable to heat. The diazonium salts prepared by Dr. Cain and Dr. Morgan were coloured and stable, and like Jacobson's compounds could be represented with a true quinonoid structure.

Dr. Lapworth pointed out that if, as this ingenious formulation indicated, one of the nitrogen atoms in the diazo-group was attached to the carbon atom in the para-position to that linked to the other nitrogen atom, it had to be assumed that the new carbon-nitrogen linking was very much more unstable than that which represented the normal link between the diazo-group and the benzene nucleus. Yet the former was represented as a single bond, whilst a double one was assumed in the latter case to account for its instability. Had Dr. Cain any explanation of the fact that during the changes of diazo-compounds nitrogen had never been found at the point where his formula suggested it should, at least occasionally, be discovered?

Dr. Cain, in reply to Dr. Lapworth, pointed out that the linking

in the group N·CH was usually a very unstable one, and in the present case was largely influenced by the condition of the linkings in the benzene nucleus.

***120. "Dibromoaminoazobenzene." By John Theodore Hewitt and Norman Walker.**

A dibromoaminoazobenzene, produced by the action of bromine on an aqueous alcoholic solution of aminoazobenzene, has been described by Berju (*Ber.*, 1884, **17**, 1403), who gives the melting point as 152° and has not determined the constitution of the compound. The present authors find that the action of bromine on an acetic acid solution of aminoazobenzene in presence of sodium acetate gives benzeneazo-*oo*-dibromoaniline, m. p. 168°. This forms the chief constituent of the product obtained by Berju's method. The *diacetyl* derivative melts at 137°, the *dibenzoyl* derivative at 229°. The constitution was determined by reduction with sodium hyposulphite, the 2 : 6-dibromo-1 : 4-phenylenediamine of m. p. 138° (E. Noelting, E. Grandmougin, and O. Michel, *Ber.*, 1892, **25**, 3334) being isolated.

121. "Phenol *p*-sulphoxide." By Samuel Smiles and Alexander William Bain.

The authors described the preparation of *phenol* p-*sulphoxide*, and showed that its properties differ widely from those assigned by Schall and Uhl (*Ber.*, 1892, **25**, 1893) to the substance obtained by the action of fused alkali hydroxide on the dyestuff rubbadin, and to which they attributed the same constitution. The condensation of phenol *p*-sulphoxide with salicylic acid yields *di*-p-*hydroxyphenylsalicylthetine*.

122. "*p*-Cresol sulphoxide and sulphide." By Samuel Smiles and Thomas Percy Hilditch.

These substances were obtained during an investigation of the action of dehydrating agents on ortho-hydroxysulphoxides. p-*Cresol sulphoxide* is formed by the interaction of *p*-cresol, aluminium chloride, and thionyl chloride. It crystallises in needles, which melt at 191° and are soluble in alcohol or hot water; it dissolves in strong sulphuric acid with a deep blue colour, but, unlike the other hydroxysulphoxides which have been prepared, this colour is not discharged by the addition of a phenolic ether (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 701). When the blue solution is mixed with water a pink solid is pre-

cipitated. The same substance was obtained by boiling the sulphoxide with phosphoryl chloride; it is soluble in aqueous alkali hydroxide, and the yellow solution on shaking with benzoyl chloride yields a colourless benzoyl derivative. The substance also furnishes a platinichloride. On account of the amorphous character of these compounds the investigation has been abandoned.

Dibenzoyl-p-*cresol sulphoxide* melts at 173°.

p-*Cresol sulphide* was prepared by reduction of the sulphoxide; it crystallises from a mixture of acetic acid and water in colourless needles, which melt at 101—103°.

123. "Molecular weight of β-naphthol in solution in solid naphthalene." By Edgar Philip Perman and John Hughes Davies.

The vapour pressures of solid naphthalene, of β-naphthol, and of isomorphous mixtures of these substances, at 70°, were estimated by aspirating a known volume of air through a glass spiral containing the solid, and determining the loss of weight. The mean vapour pressures obtained were: naphthalene, 3·751 mm. of mercury; β-naphthol, 0·1134 mm.; solid solution of 5 parts of β-naphthol to 100 parts of naphthalene, 3·592 mm.; 10 parts to 100, 3·476 mm.; 15 parts to 100, 3·380 mm. The corresponding molecular weights calculated are 151, 175, and 194 respectively. It is concluded that in dilute solutions, β-naphthol has the same molecular weight as in the gaseous state, whilst it associates in more concentrated solutions.

124. "Synthesis of hexatriene derivatives." (Preliminary note.) By Ida Smedley.

Experiments undertaken with the object of preparing a series of hexatriene derivatives by the elimination of chlorine from αα-dichloro-γ-alkyl-propylenes having led to unsuccessful results (*Proc.*, 1906, **22**, 158), the method adopted by Van Romburgh and Dorssen (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 565) for the preparation of the simplest member of the series, C_6H_8, was applied. The formate of dihydrocinnamoin was prepared; this readily resinifies and does not therefore afford a convenient method of synthesis of the pure diphenylhexatriene, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C_6H_5$.

This hydrocarbon may, however, be obtained by the condensation of phenyl*iso*crotonic acid with cinnamaldehyde in the presence of acetic anhydride. From acetone or benzene solution, it is deposited in pale

yellow crystals, melting at 194°. The dilute benzene solution exhibits a remarkable blue fluorescence.

125. "The reduction of aromatic nitro-compounds to azoxy-derivatives in acid solution." By Bernhard Flurscheim and Theodor Simon.

According to a general rule, azo- and azoxy-compounds are formed when aromatic nitro-compounds are reduced in alkaline solution, but never in presence of free mineral acids. One of the authors has, however, previously shown (*J. pr. Chem.*, 1905, [ii], 71, 497) that it is often possible to isolate the azoxy-compound in acid solution as well, sometimes even in theoretical yield, and that the above-mentioned law must be abandoned.

It was, however, further necessary to determine the conditions which favour the formation of azoxy-products or prevent it. To render this possible, an exact separation of the substances, resulting from the reduction of nitro-compounds by means of stannous chloride and hydrochloric acid in alcoholic solution, had to be effected. To this end the first part of the present research has been devoted, and the authors have succeeded in separating quantitatively the products of reduction, namely, amines, aminophenols, azoxy- and aminoazoxy-compounds from each other and from the unattacked nitro-compounds.

With the help of these new methods, more than sixty reductions have been carried out, with varying quantities of acid, and under changing conditions. The following nitro-compounds have been used: nitrobenzene, *m*-dinitrobenzene, 2:4-dinitrotoluene, 4:6-dinitro-*m*-xylene, 1-chloro-2:4-dinitrobenzene, 1-bromo-2:4-dinitrobenzene, 3:5-dichloro-4-bromonitrobenzene, 2:4-dinitrodiphenylamine, and *p*-nitrobenzaldehyde. The chief results may thus be briefly summarised:

(1) Reduction in acid, neutral, and alkaline solutions proceeds in accordance with Haber's hypothesis, nitroso- and hydroxylamino-derivatives being successively formed.

(2) The formation of azoxy-compounds during reduction is due to a condensation of hydroxylamino- and nitroso-derivatives.

(3) This condensation can only take place when the residual affinity of the tervalent nitrogen atom in the hydroxylamino-compound is not saturated.

(4) Such saturation taking place, when salts are formed anything favouring dissociation of these salts, for instance, negative substituents in the nucleus, also favours condensation, whilst increasing quantities of acid tend to prevent it.

(5) A diminution in the velocity of reduction favours condensation.

(6) Ortho-substituents diminish the velocity both of reduction and condensation; these being opposite influences, the influence of ortho-substituents on the formation of azoxy-compounds varies with their nature, some favouring condensation (bromine, &c.), others tending to prevent it (methyl, &c.).

All the results can be depicted graphically, the percentage of azoxy-compounds produced forming for each substance a curve falling with increasing quantities of acid used. In the absence of ortho-substitution, nitro-compounds with strongly negative nucleus substituents yield curves running above those obtained with less negative radicles.

126. "Action of selenium and tellurium on arsine and stibine." By Francis Jones.

In continuance of his previous work (*Journ. Chem. Soc.*, 1876, 641), where it was shown that sulphur decomposes arsine and stibine in presence of light in accordance with the equation $2SbH_3 + 6S = Sb_2S_3 + 3H_2S$, the author has now investigated the action of these hydrides on the elements analogous to sulphur, namely, selenium and tellurium, in presence and absence of light and at 100°.

The results are shown in the following table:

(a). *In sunlight.*

Element.	Hydride.	Result.	Element.	Hydride.	Result.
Sulphur	SbH_3	Reacts easily	Sulphur ...	AsH_3	Reacts slowly
Selenium.....	SbH_3	Reacts easily	Selenium ...	AsH_3	Reacts
Tellurium ...	SbH_3	Reacts	Tellurium ...	AsH_3	Reacts

(b). *At* 100°.

Sulphur	SbH_3	Reacts slowly	Sulphur ...	AsH_3	Reacts slowly
Selenium.....	SbH_3	Reacts slowly	Selenium ...	AsH_3	No action
Tellurium ...	SbH_3	Reacts very slowly	Tellurium ...	AsH_3	No action

(c). *In the dark.*

Sulphur	SbH_3	No action	Sulphur ...	AsH_3	No action
Selenium.....	SbH_3	Reacts slightly	Selenium ...	AsH_3	No action
Tellurium ...	SbH_3	No action	Tellurium ...	AsH_3	No action

It was previously shown that the facility of the decomposition of the hydrides increases with the rise in the molecular weight of these gases, phosphine being very slowly decomposed, arsine more rapidly, and stibine very rapidly. It is now found that the action of these hydrides on sulphur, selenium, and tellurium corresponds with the rise in the atomic weights of these elements, stibine being readily decomposed by sulphur, more slowly by selenium, and still more slowly by tellurium. An exception was noticed in the case of stibine, which acts on selenium even in the dark.

In the course of the investigation it was observed that arsine reacts with solution of lead acetate, producing a black precipitate, probably an arsenide of lead, the composition of which varied in different preparations.

127. "The double nitrites of mercury and the alkali metals." By Prafulla Chandra Rây.

Mercuric nitrite forms a series of double salts with the nitrites of potassium, sodium, and lithium in which 1 molecule of the former combines with 1, $1\frac{1}{2}$, 2, 3, and 4 molecules of the latter.

128. "Silver-mercuroso-mercuric hydroxynitrates and the isomorphous replacement of univalent mercury by silver." By Prafulla Chandra Rây.

When a solution containing mercuroso-mercuric nitrite and silver-mercuric nitrite is allowed to evaporate spontaneously, a series of silver-mercuroso-mercuric hydroxynitrates crystallises out. In each of these salts a part of the mercurous mercury is isomorphously replaced by silver.

129. "The molecular weights of amides in various solvents." (Preliminary note.) By Andrew Norman Meldrum and William Ernest Stephen Turner.

In the course of an investigation into the molecular condition of typical amides in various solvents, the authors have found that the molecules of trichlorolactamide, of benzanilide, and of salicylamide are associated in benzene solution even at the boiling point, and those of benzamide in benzene, in chloroform, and in acetone solution.

No case of association in alcohol solution has been discovered, acetamide, monochloroacetamide, and benzamide giving normal results. In the case of amides derived from stronger organic

acids than these, the "molecular weights" in alcohol are abnormally low.

The results obtained with water as solvent are unexpected, association being found in at least three cases, acetamide, benzamide, and salicylamide.

130. "Some experiments on the oxidising action of hydrogen peroxide." (Preliminary note.) By William Henry Perkin, jun.

During the course of researches on the constitution of brazilin and hæmatoxylin, the observation was made that certain of their derivatives, when treated with hydrogen peroxide (30 per cent.) and acetic acid, were readily oxidised with the formation of new substances the investigation of which will, it is hoped, throw much light on the constitutions of these important natural colouring matters.

Thus, for example, *brazilein*, $C_{16}H_9O_2(OH)_3$, is under these conditions converted into a substance, $C_{16}H_{14}O_9$, which crystallises in brown needles and *trimethylbrazilein*, $C_{16}H_9O_2(OMe)_3$, yields a colourless crystalline substance, $C_{19}H_{20}O_8$, which melts at 218° with decomposition. The detailed description of these and other similar oxidation experiments of brazilein and hæmatein is reserved for a subsequent communication.

Experiments of a more general nature seem to indicate that hydrogen peroxide may prove to be a reagent of considerable importance, especially in connexion with analytical researches.

It appears, for example, to react readily with αα-diketones and generally with substances possessing quinonoid structure.

Benzil is readily attacked, when its suspension in a little acetic acid is mixed with hydrogen peroxide and warmed on the water-bath, and the product contains large quantities of benzoic acid and a pale yellow oil which has not yet been investigated.

When *phenanthrenequinone* (5 grams) suspended in glacial acetic acid (15 c.c.) and hydrogen peroxide (5 c.c.) is heated at 90—95°, the crystals soon dissolve and the solution, on dilution with water, deposits 5 grams of pure diphenic acid, a method which is by far the most convenient for the preparation of this important acid.

Aurin, under similar conditions, is very readily attacked by hydrogen peroxide with formation of *p*-hydroxybenzoic acid and benzoquinone. Obviously the aurin is, in the first place, oxidised to *p*-hydroxybenzoic acid and quinol,

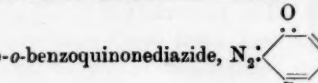
$$(C_6H_4{\cdot}OH)_2C{:}C_6H_4{:}O + 2H_2O_2 = C_6H_4(OH){\cdot}CO_2H + 2C_6H_4(OH)_2,$$

and the latter is then further oxidised to benzoquinone. It will be

shown, in a later communication, that this decomposition is of importance in connexion with the determination of the constitution of brazilein and hæmatein. The special value which appears to attach to hydrogen peroxide lies in the fact that it can be employed to oxidise phenolic substances, like brazilein and aurin, without the usual and often very laborious routine of protecting the hydroxyl groups by methylation. Experiments are in progress with the view of determining the special conditions under which hydrogen peroxide may be employed with success. The presence of acetic acid appears to be generally advantageous, but other solvents may be employed, and, in some cases, the oxidation of phenolic substances has been found to proceed well in alkaline solution.

131. "Action of hydroxylamine on *o*-benzoquinonediazides (*o*-diazophenols). 3 : 5-Dibromo-*o*-azoiminobenzoquinone (4 : 6-dibromo-2-hydroxyphenylazoimide)." (Preliminary note.) By Kennedy Joseph Previté Orton, William Charles Evans, and Emrys Morgan.

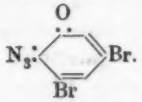
The simple means of preparing the benzoquinonediazides, especially the halogen-*o*-benzoquinonediazides, from the *s*-trihalogendiazonium salts of weak acids (Orton, *Trans.*, 1903, **83**, 796), a reaction in which a halogen atom is replaced by a hydroxyl group, has permitted of a detailed study of the behaviour of these substances with a number of reagents. The recent appearance of a paper by Forster and Fierz on "Aromatic Azoimides" (*Trans.*, 1907, **91**, 855), in which is described the preparation of *p*-hydroxyphenylazoimide from *p*-diazophenol and hydroxylamine, shows that it is advisable to make a preliminary announcement of one of the authors' results.

3 : 5-Dibromo-*o*-benzoquinonediazide, 

(Orton, *loc. cit.*), reacts very readily with hydroxylamine in alcohol solution, the reaction being completed if the hydrogen chloride of the hydroxylamine hydrochloride is replaced by a weak acid or neutralised by a base. On adding water to the resulting alcoholic solution, the *azoimide*, the yield of which is quantitative, separates in yellowish-brown needles melting at 98°, the molten material decomposing slowly a few degrees above the melting point. The azoimide is readily soluble in all organic solvents except light petroleum, and is slightly soluble in water, to which it imparts a bright yellow colour. It has a decided acid character, dissolving in solutions of alkali hydroxides and carbonates. In anhydrous solvents, it also appears to com-

bine directly with hydrogen chloride. The azoimide dissolves in sulphuric acid with the evolution of nitrogen, the solution acquiring a deep magenta colour. With bromine it yields a tetrabromoaminophenol.

Inasmuch as the azoimido-group does not in itself confer colour, whilst this compound is deeply coloured, the authors are inclined to give it provisionally a quinonoid structure, thus :



3 : 5-Dibromo-2-nitro-*p*-benzoquinonediazide and 4-bromo-*o*-naphthaquinonediazide (Orton, *loc. cit.*) react similarly with hydroxylamine.

132. "Oxime formation and decomposition in presence of mineral acids." By Arthur Lapworth.

The conversion of stable hydroximido-compounds into the corresponding ketones or aldehydes is as a rule to be effected by the use of hydrochloric acid in presence of formaldehyde. *iso*Nitrosocamphor, for example, gives an excellent yield of camphorquinone, and even camphoroxime may be partially converted into camphor by this method, which appears to be the most general hitherto discovered. The formaldehyde is converted into formic acid in the process, while the nitrogen of the oxime appears mainly as ammonium chloride.

The hydrolytic action of mineral acids on oximes appears to be a reversible one, which is possibly, in part, the explanation of the favourable influence of the formaldehyde in the above instances. When hydroxylamine, formaldehyde, and concentrated hydrochloric acid are heated together, formic acid, ammonium chloride, and methylammonium chloride are formed. When benzaldehyde is substituted for formaldehyde, benzaldoxime and, sometimes, benzonitrile, are formed. Camphorquinone yields camphorimide, and camphor gives campholenonitrile.

133. "Note on the constituents of the seeds of the Para rubber tree (*Hevea brasiliensis*)." By Wyndham Rowland Dunstan.

The kernels of the seeds of the Para rubber tree (*Hevea brasiliensis*) were examined at the Imperial Institute in 1902, and found to contain about 50 per cent. of a fixed oil, having a specific gravity 0·9302 at 15°, saponification value 206·1, and iodine value 128·3. Like linseed oil, to which it bears considerable resemblance, this oil "dried" to a transparent varnish on exposure to air, and will probably be of commercial value for the same purposes. In the future there is likely to be an enormous production of these seeds which will not be required for

planting, and their commercial utilisation is, therefore, a matter of importance (*Bull. Imp. Inst.*, 1903, 1, 156, and 1904, 2, 22).

The seed kernels, when ground with water, evolved small quantities of hydrocyanic acid and acetone, whence it appears that a cyanogenetic glucoside is present, similar to if not identical with the phaseolunatin first obtained from the beans of *Phaseolus lunatus* (Dunstan and Henry *Proc. Roy. Soc.*, 1903, 72, 285), and subsequently isolated from flax and cassava (Dunstan, Henry, and Auld, *ibid.*, 1906, 78, 145).

A mixture of enzymes was prepared from the seeds which possessed the property of hydrolysing the oil present and also olive oil. These enzymes probably include, besides a lipase-like enzyme, one capable of decomposing the cyanogenetic glucoside, since the kernels yield hydrocyanic acid by mere contact with water. The nature of the fixed oil of the cyanogenetic glucoside and of the enzymes is being fully investigated.

Van Romburgh has shown (*Ann. Jard. Bot. Buitenzorg*, 1899, 16, 15) that the leaves of *Hevea brasiliensis* also yield hydrocyanic acid and acetone when crushed with water, and Harrison has recorded the production of hydrocyanic acid under similar conditions from the seeds of the related species *Hevea pauciflora* and *Hevea confusa* (*Rep. Govt. Lab. Brit. Guiana*, 1896–1902, Part II, p. 11).

It is hoped that sufficient material will be obtainable to enable the question to be settled as to whether these related plants, as well as *Hevea brasiliensis*, contain phaseolunatin, as seems probable.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

American Chemical Society. Chemical Abstracts. Edited by *William A.* **Noyes** [and others]. Vol. I, &c. New York 1907+. (*Reference.*) From the Society.

Jahres-Bericht über die Untersuchungen und Fortschritte auf dem Gesammtgebiete der Zuckerfabrikation. Vols. I to IV. 1861–64. Edited by *C.* **Scheibler** and *K.* **Stammer.** Breslau 1863–65.
From R. A. Scott Macfie, Esq.

Rose, *Heinrich.* Ausführliches Handbuch der analytischen Chemie. Band I. Die Lehre von den qualitativen chemisch-analytischen Untersuchungen. Band II. Die Lehre von den quantitativen chemisch-analytischen Untersuchungen. pp. xiv + 968, vi + 1070 + 125. Braunschweig 1851. (*Reference.*)
Bequeathed by the late Professor Robert Warington.

Schweizer, *Victor*. The distillation of resins. Resinate lakes and pigments. Carbon pigments and pigments for typewriting machines, manifolders, &c. pp. viii + 183. ill. London [1907]. (*Recd.* 16/5/7.)
From the Publishers: Messrs. Maclaren and Sons.

II. *By Purchase.*

Association des Chimistes de Sucrerie et de Distillerie de France et des Colonies. Bulletin. Vol. XXIV, &c. Paris 1907+. (*Reference.*)

Bollettino Chimico Farmaceutico. Edited by *Arturo* **Castoldi** [and others]. Milano 1907+. (*Reference.*)

Chemisch Weekblad. Edited by *D. B.* **Centen.** Year IV, &c. Amsterdam 1907+. (*Reference.*)

Deutsche botanische Gesellschaft. Berichte. Vol. XXV, &c. Berlin 1907+. (*Reference.*)

Deutsche pharmaceutische Gesellschaft. Berichte. Year XVII, &c. Berlin 1907+. (*Reference.*)

Deutsche physikalische Gesellschaft. Berichte. Edited by *Karl* **Scheel.** Year V, &c. Braunschweig 1907. (*Reference.*)

Gesellschaft Deutscher Naturforscher und Ärzte. Verhandlungen. 78, 1906, &c. Leipzig 1907+. (*Reference.*)

Ladenburg, *A.* Vorträge über die Entwicklungsgeschichte der Chemie von Lavoisier bis zur Gegenwart. 4 Auflage. pp. xiv + 417. Braunschweig 1907. (*Recd.* 17/5/7.)

Lusk, *Graham.* The elements of the science of nutrition. pp. 326. Philadelphia 1906. (*Recd.* 18/5/7.)

Pharmaceutisch Weekblad voor Nederland. Edited by *D. B.* **Centen.** Year XLIV, &c. Amsterdam 1907+. (*Reference.*)

Pharmaceutische Centralhalle für Deutschland. Edited by *A.* **Schneider** and *P.* **Süss.** Year XLVIII, &c. Dresden 1907+. (*Reference.*)

Pharmazeutische Zeitung. Edited by *H.* **Böttger.** Year LII, &c. Berlin 1907+. (*Reference.*)

Physikalische Zeitschrift. Edited by *E.* **Riecke** and *H. Th.* **Simon.** Year VIII, &c. Leipzig 1907+. (*Reference.*)

Röttger, *H.* Lehrbuch der Nahrungsmittel-Chemie. 3 Auflage. pp. xiv + 901. ill. Leipzig 1907. (*Recd.* 31/5/7.)

Stewart, *A. W.* Stereochemistry. pp. xx + 583. ill. London 1907. (*Recd.* 1/6/7.)

At the next Ordinary Meeting, on **Thursday**, June **20th**, 1907, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated :

"Some properties of radium emanation." By A. T. Cameron and Sir W. Ramsay.

"The affinity constants of aminosulphonic acids as determined by the aid of methyl-orange." By V. H. Veley.

"Azo-derivatives of 1 : 3-diphenylbarbituric acid. Dynamic isomerism among the coloured hydrazones of 1 : 3-diphenylalloxan." By M. A. Whiteley.

"A series of coloured diazo-salts derived from *p*-aminobenzo-α-naphthalide." By G. T. Morgan and W. O. Wootton.

"Colour and constitution of azo-compounds. Part I." By J. T. Hewitt and H. V. Mitchell.

"Colour and constitution of azo-compounds. Part II." By J. T. Hewitt and H. V. Mitchell.

"The oxidation of hydrazines by free oxygen." By F. D. Chattaway.

"Calmatambin : a new glucoside." By F. L. Pyman.

"The decomposition of hyponitrous acid in presence of mineral acids." By P. C. Rây and A. C. Ganguli.

"The chemical composition of petroleum from Borneo." By H. O. Jones and H. A. Wootton.

"The synthesis of phenonaphthacridines. Trimethylphenonaphthacridines." By A. Senier and P. C. Austin.

"The condensation of aldehydes with mixtures of α-naphthol and α-naphthylamine : synthesis of 7-aryl $\begin{matrix}\alpha\text{–}N\text{–}\alpha\\ |\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-dinaphthacridines." By A. Senier and P. C. Austin.

"An improved form of apparatus for the rapid estimation of sulphates and salts of barium." By W. R. Lang and T. B. Allen.

"The determination of sugar by Fehling's solution." By W. R. Lang and T. B. Allen.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, June 20th, 1907.

Colebourn, William Arthur,

34, Camp Street, Broughton, Manchester.

Assistant Technical Chemist. Was technically educated at the Royal Technical Institute, Salford, and the Municipal School of Technology, Manchester. Was a Crace Calvert Chemical Student at the Victoria University, Manchester. Have since been respectively engaged as assistant chemist to the Clayton Aniline Co., Ltd., Manchester, on aniline colour work; followed by designing experience with a Manchester firm of chemical and general engineers. Since May last have been engaged as second chemist to Messrs. Kodak, Ltd., Harrow, near London, photographic material manufacturers.

Harold B. Dixon. D. P. Hollingworth.
C. Sordes Ellis. L. G. Radcliffe.
John Allan. *S. J. Peachey.*

Copping, Hugh Hague,

Cabourne, Caistor, Lincolnshire.

Teacher of Science, King's Hospital, Dublin. B.A. Senior Moderator in Experimental Science, Trinity College, Dublin University.

Emil A. Werner. A. L. Robinson.
Sydney Young. Wm. Caldwell.
Wm. C. Ramsden.

Cornthwaite, Robert,

Agricultural Laboratory, Halifax.

Agricultural Analytical Chemist. Lecturer and Experimenter to the Potash Syndicate; Analytical Chemist to the West Riding Farmers' Association; Huddersfield Dairy Farmers' Supply Co., Ltd.; General Lecturer before the Farmers' Associations and Clubs on milk

constituents, and also on agricultural chemistry, &c. Inventor of patent fat extractor for milk and food-stuffs analysis.

F. W. Brown. R. O. Burland.
J. Stewart Remington. *Wm. Percy Hatton.*
Alfred Sibson. *Herbert Grime.*

Cowap, Matthewman Dalton,
21, Alma Square, St. John's Wood.

Experimental Chemist to Dr. Ludwig Mond, F.R.S., Assistant Analytical Chemist to Chemical Works.

Robert N. Lennox. Bernhard Mohr.
John W. Heath. *James D. Kettle.*
Alexander Scott.

Elias, Owen Aubrey.
123, Waller Road, New Cross, S.E.

Head of Scientific Dept., Chas. Zimmermann & Co., Manufacturing Chemists. Studied Chemistry at University Coll., N. Wales, and Physics at Mason's Coll., Birmingham, now Univ. Coll. Member Scientific Research Soc., Univ. Coll., Bangor. Inventor: Bimetric Minimeter and Automatic Pipette for separation of fluids of different specific gravity.

Hermann C. T. Gardner. Robert Wm. Lindsey.
Frederic Jas. M. Page. W. H. Martindale.
F. Filmer De Morgan.

Fischer, Eugen, Ph.D.
Biebrich, a/Rh., Germany.

Technical Director of the firm of Kalle & Co., Aktiengesellschaft, Biebrich, a/Rh.

C. Duisberg. Thos. Tyrer.
B. E. R. Newlands. *Arthur. J. Webb.*
Otto Hehner.

Gledhill, Walter George,
Dersingham, Greenroyde, Halifax.

Senior Science Master, Grammar School, Gt. Yarmouth. M.A. Camb. 2nd Class Honours, Natural Science Tripos. Teacher of Science since 1902. Past 3 years at Gt. Yarmouth. Maltster's Analyst.

James Sharp. S. F. Dufton.
S. Ruhemann. J. W. Pallister.
W. Cranfield.

Jennings, John Atkinson,

61, Gleneagle Road, Streatham, S.W.

Pharmaceutist to St. Thomas's Hospital, S.E. Pharmaceutical Chemist. Desirous of keeping in touch with current chemical literature.

Arthur W. Crossley.	Alfred E. Tanner.
H. R. Le Sueur.	*Robert Wright.*
P. Haas.	*E. H. Farr.*

Jensen, Charles William Lamb,

Oakhill, Nr. Bath.

Professional Brewer and Maltster, and Scientific Adviser to the Oakhill Brewery Co. Have written a treatise on brewing and malting and taught these to numbers of pupils with chemistry and biology as applied to those industries. My reason for joining the Chemical Society is that I may still further increase my knowledge of chemistry and biology.

J. M. Collett.	A. E. Beanes.
H. J. Wiffen.	Thos. D. Lichtenstein.

G. F. Kendall.

Lloyd, Percival George,

15, Woodside Road, Kingston-on-Thames.

Chemist and Assistant Manager, Native Guano Co.'s Kingston Works, Pupil of the late Prof. Wanklyn, Analyst at Kingston Sewage Works. Eighteen years' experience in the Chemical and Bacterial treatment and utilisation of sewage.

Henry Kenwood.	Edward C. Seaton.
W. J. Dibdin.	David Sommerville.
Colin C. Frye.	*H. H. Slater.*

F. Wallis Stoddart.

Nuttall, Walter Harold,

55, Market Street, Watford, Herts.

Research Chemist. Am a Fellow of the Institute of Chemistry, and hold their special Diploma in Therapeutics, Pharmacology, Microscopy. Four years' study at the University College, Nottingham, under Prof. Kipping. One year's study at Berne University (Switzerland) under Prof. Kostanecki. Three years Head Assistant to the Nottingham City Analyst. For last 18 months, Chief Chemical Assistant at the "Cooper Research Laboratory," Watford.

F. Stanley Kipping.	J. J. Sudborough.
H. J. H. Fenton.	G. Druce Lander.

W. F. Cooper.

Pochin, Harold,

12, Chapel Street, Berkhamsted, Herts.

Assistant Schoolmaster. Graduate in Science (Honours), Cambridge University. Science Master at Berkhamsted School. I am desirous of keeping in touch with modern chemical science.

J. H. Robbins. C. Proctor.
H. W. Davis. J. Woodward.

E. Grant Hooper.

Tinkler, Charles Kenneth,

297, Franklin Road, King's Norton, Nr. Birmingham.

Lecturer and Demonstrator in Chemistry, The University, Birmingham. B.Sc. (Wales), 1st class honours in Chemistry.

Percy F. Frankland. Alexander Lauder.
James J. Dobbie. Alex. Findlay.

Hamilton McCombie.

Warner, Charles Horne,

24, Gordon Street, Gordon Square, W.C.

Demonstrator in Chemistry at the School of the Pharmaceutical Society. Pharmaceutical Chemist.

Arthur W. Crossley. Herbert Jackson.
T. E. Wallis. E. Towyn Jones.

J. E. Coates.

Young, Walter Ormston,

Springfield, Cartmel, Lancs.

Analyst. Ten years Assistant Chemist to Sir W. G. Armstrong, Whitworth & Co., Ltd. Two years First Assistant to J. Stewart Remington, Esq., Aynsome, Lancs.

J. Stewart Remington. John Hamer.
Claude Smith. *Cecil Cooke Duncan.*

R. R. Tatlock.

Zortman, Israel Hyman,

Sternwartenstr. 44 IIr, Leipzig.

Research Student. B.Sc. (Vict.). Joint paper with Prof. J. B. Cohen entitled "The Rotation of the Menthyl Esters of the Isomeric Dibromobenzoic Acids," *Trans. Chem. Soc.*, 1906. "1851 Exhibition" Scholar (Leeds University). Engaged in research work with Prof. Hantzsch, Leipzig.

Arthur Smithells. H. M. Dawson.
J. B. Cohen. W. Lowson.

C. E. Whiteley.

The following certificate has been authorised for presentation to Ballot by the Council, under Bye-law I (3).

Sahni, Ruchi Ram,
Lahore, India.

Assistant Professor of Chemistry, Government College, Lahore. M.A. in Physics and Chemistry, 1885. Assistant Professor of Chemistry, Government College, Lahore. Member of the Syndicate and Science Faculty of the Punjab University.

P. C. Rây. B. Mouat Jones.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 29/6/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 328.

Thursday, June 20th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs.:

Arthur John Banks, 61, Lawton Road, Waterloo, Liverpool.
John Kaye, M.A., B.Sc., Westerfield, Perth.
Marcus Wechsler, D.Sc., 136, Sinclair Road, Kensington, W.

Certificates have been authorised by the Council under Bye-Law I. (par 3) in favour of Messrs.:

David Leo Behrmann, 75, Sirewright Avenue, Doomfontein, Transvaal.
William Bush Schober, B.Sc., Ph.D., Lehigh Univ., South Bethlehem, U.S.A.

A Ballot for the Election of Fellows was held, and the following were subsequently declared duly elected:

William Arthur Colebourn.
Hugh Hague Copping, B.A.
Matthewman Dalton Cowap.
Owen Aubrey Elias.
Eugen Fischer, Ph.D.
Walter George Gledhill, M.A.
John Atkinson Jennings.
Charles William Lamb Jensen.
Percival George Lloyd.
Walter Harold Nuttall.
Harold Pochin, B.A.
Ruchi Ram Sahni, M.A.
Charles Kenneth Tinkler, B.Sc.
Charles Horne Warner.
Walter Ormston Young.
Israel Hyman Zortman, B.Sc.

Of the following papers, those marked * were read:

***134. "Some properties of radium emanation." By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.**

It has been discovered that the emanation from radium undergoes a rapid change of volume shortly after its change from the solid to the gaseous state; this is followed by a slow change, corresponding with its loss of electrical activity. Glass tubes, as well as silica tubes, were used for the experiments. The absorption of helium, hydrogen, oxygen, and carbon dioxide was investigated in these tubes so as to estimate the necessary corrections for the loss of volume by the emanation. It has been shown by thirty sets of measurements that the emanation behaves in accordance with Boyle's law, both before and after this preliminary change. Measurements have been made of the initial volume of the emanation, obtained from a solution of 87·7 milligrams of radium (metal) as bromide and sulphate. From these it would appear that, instead of the previously accepted value for the average-life-period of radium, 1100 years, a much shorter life must be deduced, namely, 236 years. The change of fresh emanation is accompanied by a halving of its volume, and reasons were adduced for the belief that this change corresponds with its polymerisation from Em^1 into Em^2; the change, as shown by time measurements, is a unimolecular reaction, and the subsequent rate of contraction agrees numerically with the loss of electrical activity. It has also been shown that helium, contained in silica vessels, may pass into the walls, but the conditions under which this absorption takes place have not been elucidated. Lastly, a deposit consisting doubtless of radium *D* has been observed; it is a brown substance, with a sub-metallic lustre, not easily attacked by oxygen. The half-life-period of radium *D* is said to be forty years, whilst those of radium *A*, *B*, and *C* are only a few hours.

Discussion.

Professor Clowes asked whether statements made by Dr. Thorpe that afternoon, which were supplementary to his Bakerian lecture, might not explain the presence of free hydrogen after exploding the mixture of oxygen and hydrogen arising from the decomposition of water. The lecturer had mentioned that he had invariably noticed an odour of ozone and of hypochlorite from solutions of radium bromide. If ozone were formed, this would lead to removal of oxygen by the action of the mercury in the pump, and if hypochlorite were produced, oxygen would remain combined in the solution. An excess of hydrogen would in either case remain after the explosion.

Mr. BALY asked whether it were not possible that the discrepancy between Sir William Ramsay's and Prof. Rutherford's values for the life of the radium atom could be explained by the life being shortened in the presence of the emanation. It was necessary to assume that the radium atom was in a very unstable condition and it appeared possible that its disintegration might be assisted by the bombardment due to the decomposition of the emanation. Prof. Rutherford made his observations with a very thin layer of radium bromide on a plate from which the emanation readily escaped. Sir William Ramsay on the other hand allowed the solution of radium bromide to stand for periods of four days during which time the emanation was concentrating in the solution.

In reply to a question from Prof. Rutherford, Sir W. RAMSAY stated that the emanation, when it passes from the solid to the gaseous state, passes at once into a monatomic gas, although one would imagine that a diatomic gas would be preferably formed. This may conceivably be connected with another unusual phenomenon which it displays; for at 80° the diatomic gas reverts almost entirely to its monatomic state, at 132° the reversion is not so complete, and at 237° still less complete. This is contrary to the general behaviour of compounds, yet it is not inconceivable that a higher temperature might prove favourable to combination and that a diatomic gas may be more stable at high than at low temperatures. The author, however, maintained that he was there to chronicle and not to defend the behaviour of the emanation.

The volume of helium produced from 1 volume of an emanation is about $3\frac{1}{2}$ volumes—agreeing in this respect with Prof. Rutherford's contention that the α-particle is a helium atom. In reply to Prof. Clowes, it was pointed out that no ozone is produced from a solution of radium bromide although the solid bromide has an odour of ozone.

***135. "The affinity constants of aminosulphonic acids as determined by the aid of methyl-orange." By Victor Herbert Veley.**

In continuation of a former investigation on this subject (*Trans.*, 1907, **91**, 153) the affinity constants of certain aminonaphtholsulphonic acids have been determined, and the general results are as follows.

(i) The affinity constants of the aminonaphtholsulphonic acids when determined by the tintometer method show, as regards the effect of the introduction of the hydroxyl grouping in the naphthylaminesulphonic acids, relationships similar to those observed by Ostwald by the electric conductivity method for the hydroxybenzoic acids as compared with benzoic acid.

(ii) One possible case of steric hindrance induced by the introduction of the hydroxyl grouping in the 8-position was noted.

Attempts were made to examine the naphtholsulphonic acids by the above method, but the acidic reaction appeared to be mollified by some subsequent secondary change.

***136. "Azo-derivatives of 1:3-diphenylbarbituric acid. Dynamic isomerism among the coloured hydrazones of 1:3-diphenylalloxan." By Martha Annie Whiteley.**

In order to thrown some light on the structure of the compounds obtained by the action of aromatic diazonium chlorides on the 5-alkyl-substituted derivatives of 1:3-diphenylbarbituric acid (*Proc.*, 1906, **22**, 201), the investigation has been extended, and the action of the β-substituted derivatives of phenylhydrazine on 5:5-dibromo-1:3-diphenylbarbituric acid has been examined. The results show that the compounds obtained in the first reaction are *azo*-derivatives, whilst those obtained in the second are *hydrazones*.

In the course of the investigation the following compounds have been prepared: *5-benzeneazo-5-benzyl-1:3-diphenylbarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CH_2Ph}_{N:NPh}$; *5-benzeneazo-5-diphenylmethyl-1:3-diphenylbarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CHPh_2}_{N:NPh}$; the *nitro*-derivative, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C<^{CHPh_2}_{N:N\cdot C_6N_4\cdot NO_2}$, melt and decompose at 170—171°, 160°, and 175° respectively. These compounds are yellow. *1:3-Diphenylalloxanphenylmethylhydrazone*,

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPhMe;$$

1:3-diphenylalloxandiphenylhydrazone, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPh_2$; *1:3-diphenylalloxanphenylbenzylhydrazone*,

$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>C:N\cdot NPh(CH_2Ph),$$

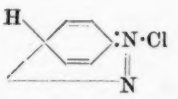
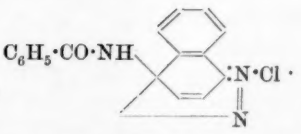
melt and decompose at 175°, 254—255°, and 130—131° respectively; these compounds exist in two forms, one yellow and one red.

***137. "A series of coloured diazo-salts derived from benzoyl-1:4-naphthylenediamine." By Gilbert Thomas Morgan and William Ord Wootton.**

The examination of the diazo-salts of benzoyl-*p*-phenylenediamine and benzoyl-1:4-naphthylenediamine has been continued and it has been found that the diazo-derivatives of the latter base are extremely stable substances which are invariably coloured.

Benzoyl-4-aminonaphthalene-1-diazonium chloride,
$C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot Cl$,
m. p. 140° with decomposition, crystallises in well-defined, yellow needles which retain their colour after repeated crystallisation from water or fractional precipitation from different organic media. The corresponding *bromide*, *iodide*, *sulphate*, *nitrate*, *nitrite*, *chlorate*, *perchlorate*, *carbonate*, *trichloroacetate*, and *thiocyanate* have been prepared. The sulphate crystallises in golden-yellow leaflets or needles, whilst the perchlorate, which is quite stable in the dry state, separates in sparingly soluble, light yellow crystals and is the palest compound of the series. These compounds have the chemical properties of diazonium salts and couple readily with alkaline β-naphthol to furnish azo-derivatives. With potassium cyanide they yield *benzoyl-4-aminonaphthalene-1-diazocyanide*, a stable, red microcrystalline compound which does not couple with alkaline β-naphthol.

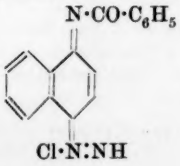
These coloured salts might be regarded either as *syn*-diazo-derivatives or as equilibrium mixtures of diazonium and *syn*-diazo-derivatives, although their great stability somewhat militates against the assumption that they consist wholly or in part of *syn*-diazo-compounds. The existence of such a series of coloured diazo-salts would be anticipated from the formulation recently suggested by Cain for diazonium salts (formula I)

(I).  (II). 

According to this view, the appearance of colour in the foregoing series may be connected with the replacement of a benzene by a naphthalene nucleus and the substitution of the hydrogen atom of formula (I) by the heavy group $C_6H_5 \cdot CO \cdot NH$ of formula (II).

Discussion.

Dr. Hewitt thought it very probable that coloured diazonium salts might possess a quinonoid structure. But as in all cases when the salts were coloured they allowed of a true quinonoid formulation, Dr. Morgan's compound might well have the constitution



whilst the constitution Dr. Morgan assigned to the salt more resembled that of the "chinols" of Bamberger, which are colourless.

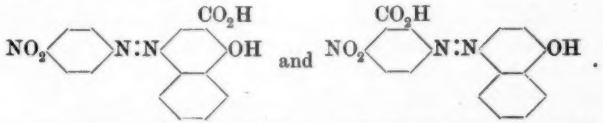
Dr. Cain thought there was much danger in speculating as to the colour of a compound entirely from the quinonoid or non-quinonoid state of only a part of the molecule. The rest of the molecule, as Dr. Morgan had pointed out, was of much importance in attempting to arrive at an explanation of the colour.

In reply, Dr. Morgan said that he preferred the formula for diazo-salts advocated by Dr. Cain to those which required the presence of a labile hydrogen atom in the para-position to the diazonium complex because the former configuration was applicable both to the simpler colourless diazonium salts and also to the more complex coloured diazo-derivatives described in this communication. The development of colour in this series of substances seemed to depend to some extent on the nature of the aromatic nucleus and partly on the presence of a complex substituent in the para-position to the diazo-nitrogen. Further experimental evidence, however, would be required before the conditions determining the appearance of colour among the diazonium derivatives could be completely defined.

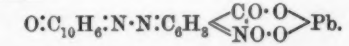
***138. "Colour and constitution of azo-compounds. Part I." By John Theodore Hewitt and Herbert Victor Mitchell.**

The authors recently drew attention to the very marked change in colour when *p*-nitro-derivatives of arylazo-*p*-phenols were dissolved in alkalis (*Trans.*, 1906, **89**, 13, 17). The explanation was offered that whilst benzeneazophenol forms alkaline salts of corresponding constitution, the *p*-nitro-derivatives furnish salts with the metal attached to the nitro-group and therefore diquinonoid in structure. The relationships are rendered apparent by the formulæ $C_6H_5\cdot N{:}N\cdot C_6H_4\cdot OK$ and $KO_2N{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O$.

Definite proof has been obtained of the correctness of this view by a comparison of the two carboxylic acids derived from *p*-nitrobenzene-azo-α-naphthol of the formulæ



Both these compounds give deep blue, alkaline solutions, but, whilst the former yields brown precipitates with salts of heavy metals, the latter gives blue precipitates; no doubt in the latter case the lead salt has the constitution



The following compounds were described:

2-Nitro-5-acetylaminobenzoic acid, m. p. 210—220° (with decomposition). *2-Nitro-5-aminobenzoic acid*, m. p. about 235°. p-*Nitro*-m-*carboxybenzeneazo-α-naphthol*, m. p. 260°. o-*Nitrobenzeneazo-α-hydroxy-β-naphthoic acid*, m. p. 200°. m-*Nitrobenzeneazo-α-hydroxy-β-naphthoic acid*, m. p. 220—225°. p-*Nitrobenzeneazo-α-hydroxy-β-naphthoic acid*, m. p. 242°. p-*Nitro*-m-*carboxybenzeneazophenol*, m. p. 195°. p-*Nitro*-m-*carboxybenzeneazo*-o-*nitrophenol*, m. p. 213°. p-*Nitro*-o-o-*dibromophenol*, m. p. 205—206°. p-*Nitrobenzeneazosalicylaldehyde*, m. p. 192—193°; its *acetyl* derivative, m. p. 150°, and *phenylhydrazone*, m. p. 235—240°. The melting points in this and the preceding papers are uncorrected, the decomposition which occurs rendering accurate observation impossible.

The general result arrived at is that the frequency of the absorbed light is lowered by increase in the length of the chain of alternate single and double linkings. The introduction of substituents may modify the length of the chain owing to the possibility of more stable salt formation in other directions.

139. "The oxidation of hydrazines by free oxygen." By Frederick Daniel Chattaway.

Hydrazines of the formula $R{\cdot}NH{\cdot}NH_2$, where R is a cyclic group, are readily oxidised by free oxygen, the action being accelerated in a remarkable way by alkali hydroxides. In the case of phenylhydrazine dissolved in about three times its weight of 4*N*-alcoholic potash, oxidation is so rapid that the liquid effervesces freely from escape of nitrogen on mere exposure to the air.

The action appears to be a general one, and results in the liberation of nitrogen and the replacement of the $NH{\cdot}NH_2$ group by hydrogen, thus: $R{\cdot}NH{\cdot}NH_2 + O = R{\cdot}H + N_2 + H_2O$.

It is simply explained by assuming that when such a hydrazine is oxidised, an unstable hydroxyhydrazine is first produced, which at once decomposes, thus: $R{\cdot}HN{\cdot}NH_2 \longrightarrow R{\cdot}HN{\cdot}NH{\cdot}OH \longrightarrow RH + N_2 + H_2O$.

The action which takes place in the oxidation of hydrazines is thus closely connected with those reactions of diazonium compounds in which the diazonium group is replaced by hydrogen.

140. "Calmatambin: a new glucoside." By Frank Lee Pyman.

The author described the isolation of a new glucoside, *Calmatambin*, from the bark of a tree indigenous to West Africa, which is known to the natives as *Calmatamba*, and is probably identical with *Canthium glabrifolium*.

The glucoside has the formula $C_{19}H_{28}O_{13},2H_2O$, and crystallises in needles melting at 100°. The anhydrous substance melts at 144—145°. It contains one methoxyl group, has $[\alpha]_D$ −130·4°, and occurs in the bark to the amount of 1·1 per cent. It is readily hydrolysed by dilute acids and by emulsin.

Octa-acetyl-calmatambin, $C_{19}H_{20}O_{13}(C_2H_3O)_8$, forms needles melting at 179—180°, and has $[\alpha]_D$ −107·1°.

Calmatambetin, $C_{13}H_{18}O_8,\frac{1}{2}H_2O$, is formed together with dextrose by the action of emulsin on calmatambin according to the equation $C_{19}H_{28}O_{13} + H_2O = C_6H_{12}O_6 + C_{13}H_{18}O_8$. It crystallises in needles melting at 148—149°. It contains one methoxyl group and is optically inactive. It is readily decomposed by the action of dilute acids, and yields a small amount of a scarlet, crystalline *substance*, $C_{11}H_{12}O_3$, melting at 91°, which is volatile with steam, and has an aromatic odour; it may very possibly be a quinone.

The foregoing results show that calmatambin is a β-glucoside, having the constitution represented by the formula

$$CH_3{\cdot}O{\cdot}C_{12}H_{10}O_2(OH)_4{\cdot}O{\cdot}C_6H_{11}O_5.$$

Calmatambin is devoid of any appreciable physiological action.

141. "The decomposition of hyponitrous acid in presence of mineral acids." By Prafulla Chandra Rây and Atul Chandra Gañguli.

Hyponitrous acid, when liberated from silver or mercurous hyponitrite by the action of dilute nitric, hydrochloric, or sulphuric acid at 25° or a higher temperature, decomposes at once according to the following equations:

$$(1)\ 2HNO = H_2O + N_2O.$$
$$(2)\ 5HNO = 2H_2O + HNO_3 + 4N.$$

Neither nitrous acid, ammonia, or hydroxylamine is formed. The presence of the mineral acids has a specific directive influence in determining the course of reaction.

142. "The chemical composition of petroleum from Borneo." By Humphrey Owen Jones and Hubert Arthur Wootton.

The petroleum from Borneo has been found to consist of approximately equal quantities of homologous hydrocarbons of the paraffin, *cyclo*hexane, and aromatic series, and to contain the members of the naphthalene series to the extent of about 6—7 per cent. The less volatile portions of the oil are optically active.

It forms a very convenient source of the nitro- and amino-derivatives of the aromatic hydrocarbons, which may be obtained in large quantities and in a highly pure state.

143. "The synthesis of phenonaphthacridines: trimethylphenonaphthacridines." By Alfred Senier and Percy Corlett Austin.

The authors have employed the methylene di-iodide and arylamine method (Senier and Goodwin, *Trans.*, 1902, **81**, 280) for the synthesis of phenonaphthacridines by using equimolecular mixtures of ψ-cumidine and naphthols, and good yields of the two desired trimethylphenonaphthacridines were obtained. When the naphthylamines were used in place of the naphthols, the product generally contained the corresponding dinaphthacridine.

The condensation of trioxymethylene with ψ-cumidine and the naphthols effected the synthesis of the same two compounds, but in this case the yields were smaller and the products less easily purified.

8 : 9 : 11-*Trimethylpheno-* $\begin{matrix}\mathrm{N}\text{—}\alpha\\ |\\ \mathrm{CH}\text{-}\beta\end{matrix}$*-naphthacridine*,

$$C_6HMe_3\left\langle\begin{matrix}\mathrm{N}-\\ |\\ \mathrm{CH}\end{matrix}\right\rangle C_{10}H_6,$$

is obtained by condensation of methylene di-iodide with ψ-cumidine and α-naphthol. It crystallises from alcohol in greenish-yellow needles melting at 160° (162·5° corr.); its solutions are fluorescent.

The *platinichloride*, *aurichloride*, *mercurichloride*, *picrate*, and *bistrimethylphenonaphthacridine hexabromide* were described.

8 : 9 : 11-*Trimethylpheno-* $\begin{matrix}\mathrm{N}\text{—}\beta\\ |\\ \mathrm{CH}\text{-}\alpha\end{matrix}$*-naphthacridine*, isomeric with the above, was obtained in a similar manner, using β-naphthol instead of α-naphthol. It crystallises from alcohol in straw-coloured needles, melting at 136° (137° corr.), and its solutions are very faintly fluorescent.

The *hydriodide*, crystallising from aniline in orange needles, appeared as an intermediate product in the preparation of the base. The *platinichloride*, *aurichloride*, *and picrate* were also described.

144. "The condensation of aldehydes with mixtures of α-naphthol and α-naphthylamine: synthesis of 7-aryl- $\begin{matrix}\alpha\text{-}\mathrm{N}\text{—}\alpha\\ |\\ \beta\text{-}\mathrm{CH}\text{-}\beta\end{matrix}$**-dinaphthacridines." By Alfred Senier and Percy Corlett Austin.**

In continuation of the study of dinaphthacridines, the authors have found that certain general differences, which they ascribe to steric influence, dependent on the position of the angular rings (compare Hinsberg, *Ber.*, 1902, **36**, 4051) between the bases of the type $\begin{matrix}\alpha\text{–}\mathrm{N}\text{—}\alpha\\ |\\ \beta\text{-}\mathrm{CH}\text{-}\beta\end{matrix}$ and those of the type $\begin{matrix}\beta\text{-}\mathrm{N}\text{—}\beta\\ |\\ \alpha\text{–}\mathrm{CH}\text{-}\alpha\end{matrix}$ are well illustrated by a detailed investigation of the aldehyde, naphthol, and naphthylamine-

method of synthesis, first introduced by Ullmann and Fetvadjian (*Ber.*, 1903, **36**, 1027).

Trioxymethylene does not yield the $\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-dinaphthacridine, whereas it readily forms the $\begin{matrix}\beta\text{-}N\text{—}\beta\\ \alpha\text{–}CH\text{-}\alpha\end{matrix}$-isomeride; benzaldehyde gives the 7-phenyl derivative of both types, and from *m*-nitrobenzaldehyde was obtained 7-*m*-nitrophenyl-$\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-dinaphthacridine, whereas Haase (*Ber.*, 1903, **36**, 593) found that with β-naphthol and β-naphthylamine it gave a dihydro-derivative of the corresponding dinaphthacridine, which could not be oxidised to the base.

From anisaldehyde and the three tolualdehydes, only derivatives of the $\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-type could be obtained. It was also noticed that in the preparation of dinaphthacridines of this type, hydro-derivatives were never formed.

7-o-*Tolyl*-$\begin{matrix}\alpha\text{-}N\text{—}\alpha\\ \beta\text{–}CH\text{-}\beta\end{matrix}$-*dinaphthacridine* is obtained in yellow crystals melting at 212° (215° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.

7-m-*Tolyl*-$\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{–}CH\text{-}\beta\end{matrix}$-*dinaphthacridine* is a yellow, crystalline powder melting at 251° (257° corr.), and gives a *platinichloride*, *aurichloride* and *picrate*.

7-p-*Tolyl*-$\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-*dinaphthacridine* forms pale greenish-yellow, rhombohedral crystals melting at 221° (224° corr.), and gives a *platinichloride*, *aurichloride*, and *picrate*.

7-p-*Methoxyphenyl*-$\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-*dinaphthacridine* crystallises from benzene in small, yellow rhombohedra melting at 257° (263° corr.), and forms a *platinichloride*, *aurichloride*, and *picrate*.

7-m-*Nitrophenyl*-$\begin{matrix}\alpha\text{–}N\text{—}\alpha\\ \beta\text{-}CH\text{-}\beta\end{matrix}$-*dinaphthacridine* crystallises from benzene in small, yellow crystals which did not melt below 300°; no sign of fluorescence was observed in any of its solutions. The *platinichloride*, *aurichloride*, and *picrate* were prepared.

145. "An improved form of apparatus for the rapid estimation of sulphates and salts of barium." By William Robert Lang and Thomas B. Allen.

N. Tarugi and G. Bianchi (*Gazzetta*, 1906, **36**, i, 347) have described an apparatus for the rapid estimation of sulphates and salts of barium by a volumetric method based on the rapid clearing of turbid solutions in tubes of narrow calibre. Their apparatus is somewhat complicated, and the authors have simplified it materially. The solution containing the precipitated barium sulphate is forced, by air pressure applied by hand, up a narrow tube, allowed to clear—which it does rapidly as the end-point of the reaction is approached—and a drop of the precipitant added. Any milkiness is plainly observed in the narrow tube, and the solution is washed down into the flask and fresh portions forced up the tube from time to time until further addition of the reagent causes no change. Experiments were made with solutions of sulphuric acid of various concentrations, with the sulphates of copper and of nickel, and also with iron pyrites to determine its sulphur content. The errors, as compared with the gravimetric estimation of sulphur as barium sulphate, range from 1 to 0·1 per cent., but such errors are materially reduced by taking the average of five or six titrations, and the whole operation can be completed in less than an hour.

146. "The determination of sugar by Fehling's solution." By William Robert Lang and Thomas B. Allen.

The apparatus described by the authors (preceding paper) for the estimation of sulphuric acid and sulphates, based on the principle of the rapid clearing of turbid solutions in tubes of narrow calibre, was employed for the determination of dextrose by means of Fehling's solution. Accurate results were obtained when the solution was heated to its boiling point, the concentration being not more than 0·15 gram in 75—100 c.c. of water, and the time of heating being five minutes. Under these conditions the average error varied from 0·1 to 0·30 per cent., but when the solutions were greatly diluted or the time of heating extended from ten to twenty minutes the results varied more than 1 per cent.

147. **"Studies in asymmetric synthesis. VI. The asymmetric synthesis of the optically active tartaric acids." By Alexander McKenzie and Henry Wren.**

The asymmetric synthesis of *l*-tartaric acid was accomplished in three ways.

(1) By the oxidation of *l*-bornyl fumarate in glacial acetic acid solution by potassium permanganate, according to the scheme:

$$\underset{\text{(Inactive.)}}{\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2\cdot C_{10}H_{17}\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ |\\ CH(OH)\cdot CO_2\cdot C_{10}H_{17}\end{matrix}} \longrightarrow$$

$$\underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2K\\ |\\ CH(OH)\cdot CO_2K\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}}.$$

(2) By the oxidation of the potassium salt of *l*-bornyl hydrogen fumarate in aqueous solution by potassium permanganate, thus:

$$\underset{\text{(Inactive.)}}{\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2K\end{matrix}} \longrightarrow$$

$$\underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ |\\ CH(OH)\cdot CO_2K\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2K\\ |\\ CH(OH)\cdot CO_2K\end{matrix}} \longrightarrow \underset{\text{(Lævorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}}.$$

In these two cases the change $\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}$ (inactive) $\longrightarrow$ $\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}$ (active) is rendered possible by the introduction and subsequent complete elimination of the *l*-bornyl group.

(3) By the oxidation of *l*-menthyl fumarate in an analogous manner.

The asymmetric synthesis of *d*-tartaric acid was accomplished by the oxidation of the potassium salt of *d*-bornyl hydrogen fumarate, thus:

$$\underset{\text{(Inactive.)}}{\begin{matrix}CH\cdot CO_2H\\ \|\\ CH\cdot CO_2H\end{matrix}} \longrightarrow \underset{\text{(Dextrorotatory.)}}{\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2H\end{matrix}} \longrightarrow \underset{\text{(Dextrorotatory.)}}{\begin{matrix}CH\cdot CO_2\cdot C_{10}H_{17}\\ \|\\ CH\cdot CO_2K\end{matrix}} \longrightarrow$$

$$\underset{\text{(Dextrorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2\cdot C_{10}H_{17}\\ |\\ CH(OH)\cdot CO_2K\end{matrix}} \longrightarrow \underset{\text{(Dextrorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2K\\ |\\ CH(OH)\cdot CO_2K\end{matrix}} \longrightarrow \underset{\text{(Dextrorotatory.)}}{\begin{matrix}CH(OH)\cdot CO_2H\\ |\\ CH(OH)\cdot CO_2H\end{matrix}}.$$

148. "Some derivatives of 2-phenyl-1:3-naphthylenediamine. Part I." By Norman Lees and Jocelyn Field Thorpe.

The β-amino-group in 2-phenyl-1 : 3-naphthylenediamine is more strongly basic than the amino-group in the α-position, and is the one first acted on in salt formation, diazotisation, and acetylation. Derivatives of the base, in the formation of which the β-amino-group takes part, can therefore be prepared directly from the base itself, whereas, since the β-amino-group can be readily protected by acetylation, those compounds which are derived from the amino-group in the α-position can be prepared from the monoacetyl derivative of the base.

2-Phenyl-1:3-naphthylenediamine combines with diazonium salts, forming azo-compounds, the azo-group entering in the position 4 in the naphthalene ring. The colours of these compounds do not differ appreciably in shade from those of the corresponding compounds derived from 1 : 3-naphthylenediamine; hence the presence of the phenyl group has little or no effect on the colour of compounds of this type.

Typical derivatives of the base have been prepared and investigated. The conditions have also been determined under which it is converted into the corresponding dinaphthol and the two aminonaphthols.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Chemical Trade Journal. Edited by *George E.* **Davis.** Vols. I to XI. Manchester 1887–1892. (*Recd.* 14/6/7.)

From Dr. C. E. Fawsitt.

Chemiker Zeitung. Edited by *G.* **Krause.** Year VI. Cöthen 1882. (*Recd.* 10/6/7.) From A. Esilman, Esq.

Herrick, *Rufus Frost.* Denatured or industrial alcohol. A treatise on the history, manufacture, composition, uses, and possibilities of industrial alcohol in the various countries permitting its use, and the laws and regulations governing the same. pp. x + 516. ill. New York 1907. (*Recd.* 19/6/7.)

From the Publishers: Messrs. John Wiley and Sons.

Jahrbuch der Chemie. Edited by *Richard* **Meyer.** Year I. 1891. Frankfurt 1892. (*Recd.* 5/6/7.) From J. Tudor Cundall, Esq.

Journal für praktische Chemie. Edited by *Hermann* **Kolbe** and *Ernst von* **Meyer.** New series. Vols. XXIII to XXVIII. Leipzig 1881—1883. (*Recd.* 12/6/7.)

From Geh. Rath Professor Dr. Liebermann.

THE LIBRARY.

The Library will be closed throughout the month of August, when the Society's Rooms will be redecorated, and the annual revision of the volumes will take place.

Fellows are particularly requested to return all Library Books in their possession *not later than Wednesday, July 31st*

LIST OF FELLOWS, 1907.

The List of Fellows for 1907 is now in active preparation, and changes of address *received after 31st July cannot be included in it.*

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

At the next Ordinary Meeting, on **Thursday**, July **4th**, 1907, at **8.30** p.m., the following papers will be communicated :

"*iso*Nitroso- and nitro-dimethyldihydroresorcin." By P. Haas.

"The structure of carbonium salts." By F. Baker.

"Studies of dynamic isomerism. Part VI. The influence of impurities on the mutarotation of nitrocamphor." By T. M. Lowry and E. H. Magson.

"The relation between absorption spectra and chemical constitution. Part VIII. The phenyl hydrazones and osazones of α-diketones." By E. C. C. Baly, W. B. Tuck, E. G. Marsden, and M. Gazdar.

"Permanganic acid." By M. M. P. Muir.

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Issued 13/7/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 329.

Thursday, July 4th, 1907, at 8.30 p.m., Sir ALEXANDER PEDLER, C.I.E., F.R.S., Vice-President, in the Chair.

Messrs M. D. Cowap, H. McCombie, O. A. Elias, and S. F. Stell were formally admitted Fellows of the Society.

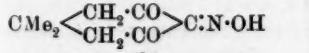
Certificates were read for the first time in favour of Messrs.:

Benjamin Owen Jones, Boksburg, Transvaal.
Thomas Callan, B.Sc., 22, Church Street, Egremont, Cheshire.
Robert Harry Smith, Apsley House, Priory Road, Sheffield.

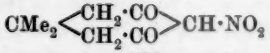
Of the following papers, those marked * were read:

*149. "*iso*Nitroso- and nitro-dimethyldihydroresorcin." By Paul Haas.

When an ice-cold aqueous solution of the potassium salt of dimethyldihydroresorcin mixed with potassium nitrite is acidified, a pale yellow precipitate of iso*nitrosodimethyldihydroresorcin* (I):



(I.)

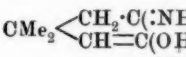


(II.)

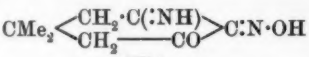
is obtained. That this substance is in reality an *iso*nitroso-derivative and not a nitroso-derivative is shown by the fact that it does not give

Liebermann's reaction, but on the contrary yields coloured *potassium*, *ammonium*, and *ferrous* salts after the manner of α-oximino-ketones. When *iso*nitrosodimethyldihydroresorcin suspended in ether is saturated with oxides of nitrogen, prepared from nitric acid and arsenious oxide, it is converted into *nitrodimethyldihydroresorcin* (II); this substance may also be prepared in a similar manner from dimethyldihydroresorcin itself.

The base (III), obtained by the action of ammonia on dimethyldihydroresorcin (*Trans.*, 1906, **89**, 191):

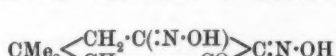


(III.)



(IV.)

when suspended in water and treated with nitrous acid at 0°, yields an *iso*nitroso-derivative of the formula (IV), which gives a crimson *potassium* salt and a blue *ferrous* salt. Both *iso*nitroso- (I) and nitrodimethyldihydroresorcin (II) on reduction yield an amine which is converted by nitrous acid into a substance of the formula $C_8H_{10}O_2N_2$. That nitrous acid in acting on the base (III) really attacks the carbon atom in the para-position relative to the two methyl groups, and not the imino-group, is shown by the fact that this *iso*nitroso-derivative (IV) yields on reduction and subsequent treatment with nitrous acid the same substance, $C_8H_{11}ON_3$, as is obtained by a similar series of reactions from the *mono-oxime* of *iso*nitrosodimethyldihydroresorcin (V):



(V.)

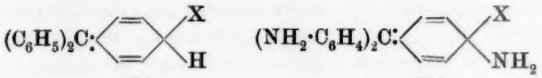
in which the nitrogen atoms are clearly attached to different carbon atoms.

***150. "The structure of carbonium salts." By Frank Baker.**

The author has examined the absorption spectra of the sulphates of several derivatives of benzylideneacetone, and also of triphenyl- and trianisyl-carbinol sulphates. These carbonium salts gave rise to two characteristic types of absorption.

p-Rosaniline base, as well as the mono-hydrochloride, shows the first type of curve, whilst in presence of more concentrated acid the second of these types of spectra is observed. From these results, the author concluded that the magentas are carbonium salts, similar to triphenylcarbinol sulphate.

Since Gomberg (*Ber.*, 1907, **40**, 1847) has shown that the latter compound possesses the structure (I):



(I.) (II.)

the constitution (II) was ascribed by the author to the salts of *p*-rosaniline with one equivalent of acid.

The second of the above-mentioned types of curve is similar to those of the hydrochlorides of certain members of the hydroxyazo-group (Tuck, *Trans.*, 1907, **91**, 449), and the author suggested that these salts are also carbonium compounds.

The absorption spectrum of triphenylmethane was found to differ from that previously described by Hartley (*Trans.*, 1887, **51**, 152).

Discussion.

Dr. Cain mentioned that Gomberg himself, in the paper quoted by the author, adopted Nietzki's formula $(NH_2 \cdot C_6H_4)_2C{:}<\!=\!>NH_2X$ for the salts of *p*-rosaniline. In view of the work of Hantzsch and Osswald and other chemists, which was generally considered to establish the correctness of Nietzki's formula, it was not likely that Mr. Baker's suggestion would be accepted by colour chemists, particularly as it seemed so improbable that the acidic group X should be attached to the carbon and not to the nitrogen atom.

Dr. Hewitt saw no necessity to ascribe a carbonium formula to the salts of hydroxyazo-compounds with mineral acids. Chemical reactions pointed to their substances having a quinonoid structure, but it was the phenolic nucleus which apparently becomes altered.

In reply, Mr. Baker pointed out that Gomberg had suggested that in the formation of magenta from *p*-rosaniline base a carbinol corresponding to the salt of the structure shown by (II) was first formed, and that this compound passed into the iminoquinone, but no proof of the latter change had been presented.

***151. "Studies of dynamic isomerism. Part VI. The influence of impurities on the mutarotation of nitrocamphor." By Thomas Martin Lowry and Egbert Hochey Magson.**

The velocity of mutarotation of nitrocamphor has been measured in a number of different solvents and in presence of a variety of added impurities.

In the experiments on glucose described in the first paper of this

series (*Trans.*, 1903, **83**, 1314), it was found that the mutarotation in aqueous solutions could not be retarded by the addition of either acid or alkali, and appeared to be due to a direct interaction between the sugar and the solvent. In the case of nitrocamphor dissolved in chloroform, however, it has been found possible to retard the isomeric change by the addition of small quantities of acid, thus confirming the view already arrived at (*Trans.*, 1899, **75**, 221) that the mutarotation of the nitrocamphor in solvents such as chloroform and benzene is conditioned by the presence of alkaline impurities.

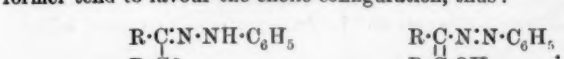
Sodium ethoxide added to an alcoholic solution of nitrocamphor was found to produce an acceleration very similar to that which results from the addition of potassium hydroxide to an aqueous solution of glucose. Extraordinary effects were produced, however, by the addition of piperidine to solutions of nitrocamphor in benzene or chloroform. In presence of *N*/1000 piperidine no mutarotation could be detected; with *N*/10,000 piperidine the mutarotation was complete in five minutes, with *N*/100,000 in an hour, and with *N*/1,000,000 in about ten hours; with *N*/10,000,000 piperidine the acceleration was of the same order of magnitude as that due to the trace of impurity normally present in the purified materials.

Discussion.

Mr. W. A. Davis, replying to the question raised by Dr. Lowry as to the origin of the peculiar odour noticed in the chloroform solutions used, suggested that it was due to carbonyl chloride formed by the action of the air on the chloroform. It would appear that this change was accelerated by the presence of an acid, in this case trichloroacetic acid; it was already well known that it could be prevented by having an alkali present such as lime.

***152. "The relation between absorption spectra and chemical constitution. Part VIII. The phenylhydrazones and osazones of α diketones." By Edward Charles Cyril Baly, William Bradshaw Tuck, Effie Gwendoline Marsden, and [in part] Maud Gazdar.**

From a consideration of their absorption spectra it was shown that the phenylhydrazones and osazones of the α-diketones in neutral solution possess the ketonic constitution, and that in alkaline solution the former tend to favour the enolic configuration, thus:



Neutral solution. Alkaline solution.

In the phenylhydrazones of hydroxy-ketones in which the hydroxyl group is adjacent to the :C:N· linking, direct evidence is found of the mutual influence of the hydroxyl group and the C:N linking. This influence is best shown in the great retardation of the change of the hydrazone to the azo-form in light; moreover, it is this mutual influence which renders possible the oxidation of the hydroxyl group by excess of phenylhydrazine. Inasmuch as the change to the azo-form removes this influence upon the hydroxyl group, this change tends to restrain the oxidation of the hydroxyl group by phenylhydrazine, and as, further, acetic acid retards the change to the azo-form, so the presence of acetic acid aids the formation of the osazones with excess of phenylhydrazine.

153. "Permanganic acid." By Matthew Moncrieff Pattison Muir.

By adding the equivalent quantity of dilute sulphuric acid to a solution of barium permanganate, filtering through glass wool, and evaporating over sulphuric acid in a vacuum, solutions of permanganic acid, $HMnO_4$, containing about 17 per cent. of the acid, can be obtained. A small quantity of a fairly concentrated solution of this acid, when left in an open vessel, deposits brown oxides of manganese ($xMnO_2$, $yMnO$, where $x = 20$ and y varies from 6 to 10), mixed with violet-blue crystals of the acid. The latter could not be obtained as a solid except mixed with oxides of manganese. A very dilute solution of permanganic acid can be boiled without decomposition; a solution containing about 4 per cent. of the acid deposits a brown film on glass on keeping for half an hour. More concentrated solutions decompose gradually with evolution of ozonised oxygen; when evaporated to dryness over sulphuric acid in a vacuum, they give black, almost pure, manganese dioxide.

154. "Methyl dicarboxyaconitate." By Siegfried Ruhemann.

The author has found that the esters of dicarboxyaconitic acid are not produced in a manner similar to the formation of ethyl dicarboxyglutaconate, namely, by the action of the esters of trichloroacetic acid on ethyl sodiomalonate, but methyl dicarboxyaconitate,

$$CO_2Me\cdot C{:}C(CO_2Me)_2\cdot CH(CO_2Me)_2,$$

was prepared according to the directions of Auschütz and Deschauer (*Annalen*, 1906, **347**, 3).

Phenylhydrazine reacts with the ester at the ordinary temperature to yield the *additive* product $CO_2Me\cdot C(NH\cdot NH\cdot C_6H_5)[CH(CO_2Me)_2]_2$ (colourless prisms, m. p. 135°). This is fairly stable, but is decomposed when it is digested with dilute caustic potash or boiled with

sodium carbonate with formation of malonic acid and *monomethyl phenylpyrazolonedicarboxylate* (colourless prisms which melt and decompose at 201—202°). The author considers that the formula of this ester is $C_6H_5\cdot N<\begin{matrix}N=C\cdot CO_2H\\ CO\cdot CH\cdot CO_2Me\end{matrix}$. On boiling with concentrated, aqueous potassium hydroxide, it furnishes potassium 1-phenyl-5-pyrazolone-3-carboxylate, $C_6H_5\cdot N<\begin{matrix}N=C\cdot CO_2K\\ CO\cdot CH_2\end{matrix}$.

At 100°, phenylhydrazine and methyl dicarboxyaconitate form, besides methyl malonate, the compound $C_{24}H_{24}O_4N_6$. This, with dilute hydrochloric acid, yields phenylhydrazine hydrochloride and the *phenylhydrazide* of *monomethyl phenylpyrazolonedicarboxylate*,

$$C_6H_5\cdot N<\begin{matrix}N=C\cdot CO_2Me\\ CO\cdot CH\cdot CO\cdot NH\cdot NH\cdot C_6H_5\end{matrix} \text{ or}$$

$$C_6H_5\cdot N<\begin{matrix}N=C\cdot CO\cdot NH\cdot NH\cdot C_6H_5\\ CO\cdot CH\cdot CO_2Me\end{matrix}$$

(colourless needles which decompose on heating).

The compound $C_{24}H_{24}O_4N_6$ therefore is the *phenylhydrazine* salt of this substance.

Methyl dicarboxyaconitate, on being heated with aniline at 100°, is decomposed, and furnishes *carboxymethylanilinomethylenemalonanil*, $CO_2Me\cdot C(NH\cdot C_6H_5):C<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_6H_5$ (canary-yellow prisms, m. p. 194°).

155. "The action of heat on α-hydroxycarboxylic acids. Part III. *aa'*-Dihydroxysebacic acid and its diacetyl derivative." By Henry Rondel Le Sueur.

The author has now extended his investigation of the action of heat on α-hydroxy-acids to the hydroxy-derivatives of dibasic acids. When *aa'*-dihydroxysebacic acid or its diacetyl derivative is heated at 250—270°, it decomposes with evolution of carbon monoxide and formation of the dialdehyde of suberic acid:

$$CO_2H\cdot CH(OH)\cdot[CH_2]_6\cdot CH(OH)\cdot CO_2H \longrightarrow CHO\cdot[CH_2]_6\cdot CHO.$$

156. "Dihydroxyadipic acids. (Preliminary note.)" By Henry Rondel Le Sueur.

When the bromine atoms in *aa'*-dibromoadipic acid are replaced by hydroxyl groups, two dihydroxyadipic acids are obtained, one melting at 146° and the other at 174°. Both form insoluble, crystalline silver

salts, and when the acid melting at 146° is heated, it loses water with formation of a dilactone which sublimes in well-defined plates.

As $\alpha\alpha'$-dihydroxyadipic acid contains two asymmetric carbon atoms, it is probable that the above acids are stereoisomerides.

157. "The relation between absorption spectra and optical rotatory power. Part II. The tartaric acids." By Alfred Walter Stewart.

The absorption spectra of the two active forms of tartaric acid are identical, and show only slight general absorption. When an equimolecular mixture of the two antipodes containing the same weight of acid as in the previous cases is used, a greater general absorption is found, proving that racemic acid has a greater power of absorption than either active form. When the racemic acid solution is diluted, however, its absorptive power gradually approximates to that of the active acids, with which it eventually becomes identical. This shows that in dilute solution the racemic acid is broken down into the two active forms, as has already been suspected from results obtained in freezing point, boiling point, and vapour density determinations. These spectroscopic results were corroborated by somewhat similar ones obtained with the active limonenes and dipentene. As a double salt above and below its temperature of transition furnishes the closest parallel to a solution which may contain either a mixture of two antipodes or a racemic compound, the spectrum of astrakanite above and below 22° was examined. It was found that above this temperature an absorptive power was shown differing from that observed below 22°, so that the two cases are evidently analogous. This also furnishes a new method of determining transition temperatures. It was found that *i*-tartaric acid had the strongest absorptive power of all, being much more absorbent than racemic acid. No absorption bands were found in any of the spectra. Applications of this work to various questions, such as the determination of existence limits in the case of racemic compounds, the proof of the actual formation of a liquid racemic compound (as distinct from an inactive equimolecular mixture), and the existence of pseudo-racemic compounds were discussed.

158. "Experiments on the synthesis of the terpenes. Part XI. Synthesis of 4-*iso*propylidene*cyclo*hexanone and its derivatives." By William Henry Perkin, jun., and John Lionel Simonsen.

The sodium derivative of ethyl α-acetylglutarate,

$$CO_2Et\cdot CHNa(COMe)CH_2\cdot CH_2\cdot CO_2Et,$$

reacts readily with ethyl β-iodopropionate with the formation of *ethyl γ-acetylpentane-αγε-tricarboxylate*,

$$CO_2Et\cdot C(COMe)(CH_2\cdot CH_2\cdot CO_2Et)_2,$$

which distils at 217° (15 mm.), and on hydrolysis with hydrochloric acid is converted into *γ-acetylpimelic acid*, $COMe\cdot CH(CH_2\cdot CH_2\cdot CO_2H)_2$. This acid is a colourless syrup which yields a *semicarbazone* melting at 177°. When ethyl γ-acetylpimelate is treated with magnesium methyl iodide, it is converted into the lactone of *ethyl hydrogen γ-isopropenolpimelate*, $\begin{matrix} Me_2C\cdot CH(CH_2\cdot CH_2\cdot CO_2Et)CH_2 \\ O\text{———}CO\text{———}CH_2 \end{matrix}$, which distils at 200° (22 mm.), and yields, with hydrobromic acid, *ethyl hydrogen γ-(bromoisopropyl)pimelate*,

$$Me_2CBr\cdot CH(CH_2\cdot CH_2\cdot CO_2Et)CH_2\cdot CH_2\cdot CO_2H.$$

Ethyl γ-(*bromoisopropyl*)*pimelate*, $Me_2CBr\cdot CH(CH_2\cdot CH_2\cdot CO_2Et)_2$, obtained by the esterification of the latter compound, is decomposed by pyridine with formation of *ethyl γ-isopropylidenepimelate*, $Me_2C{:}C(CH_2\cdot CH_2\cdot CO_2Et)_2$ (b. p. 168° under 13 mm.), and, on hydrolysis, yields *γ-isopropylidenepimelic acid*, which crystallises in prisms and melts at 97°. *Ethyl* 4-iso*propylidene*cyclo*hexanone*-2-*carboxylate*, $Me_2C{:}C\begin{matrix} CH_2\cdot CH_2 \\ \\ CH_2\cdot CH\cdot CO_2Et \end{matrix}\!\!>\!CO$, is obtained when the solution of ethyl *γ-iso*propylidenepimelate in toluene is treated with sodium; it decomposes on distillation, combines with hydrogen bromide to form *ethyl* 4-*β-bromoisopropyl*cyclo*hexanone*-2-*carboxylate*, and is hydrolysed by alcoholic potash with formation of 4-iso*propylidene*cyclo*hexanone*, $Me_2C{:}C\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!CO$.

This ketone distils at 219—221° and yields a *semicarbazone* which melts at 201°; hydrobromic acid converts it into 4-*β-bromoisopropyl*-cyclo*hexanone*, $Me_2CBr\cdot CH\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!\!>\!CO$.

The object of this research was to endeavour to synthesise nopinone, $CH\begin{matrix} CH_2\cdot CH_2 \\ \diagup\ CMe_2\ \diagdown \\ CH_2\text{—}CH \end{matrix}\!\!>\!CO$, from the above bromo-ketone by the elimination of hydrogen bromide, but the experiments which were made in this direction have so far been unsuccessful.

159. "The purification of acetic ester." By John Kenneth Harold Inglis and Lottie Emily Knight.

Great difficulty has always been experienced in preparing pure acetic ester, and although several methods have been suggested, no

one of them is satisfactory since the yield of pure ester is small and the process of preparing it laborious. For the preparation of aceto-acetic ester, very nearly pure acetic ester is required, and the presence of a moderate quantity of alcohol—the most likely impurity—is fatal to success. A series of experiments has shown that the separation can be most easily carried out by first converting the alcohol into an ester of high boiling point and then distilling. If the crude ester, as obtained in the ordinary continuous process, is dried over potassium carbonate (which also removes any acetic acid) and treated with phosphoric oxide, a slow action takes place with the formation of phosphoric esters which are neither volatile nor decomposed at the boiling point of ethyl acetate (77·20° corr.). In this way a yield of 160 grams of ester boiling within one degree was obtained in an experiment in which the theoretical yield was 264 grams, that is, 60 per cent. of ester was obtained pure.

This process, however, is slow, and requires several days for completion at the ordinary temperature. On the other hand, the removal of the alcohol takes place more rapidly at the boiling point. Thus a mixture of 100 grams of ester (b. p. 76·65—77·15°) with 8 grams of absolute alcohol distilled continuously between 73° and 77°, only 21 grams passing over above 76·3°. When, however, the fractions had been mixed together and heated for half an hour with 10 grams of phosphoric oxide, using a reflux condenser, a single distillation gave 72 grams of distillate between 76·7° and 77·2°, that is, 72 per cent. of an approximately pure substance. This result shows that it is easy to obtain by this method a good yield of acetic ester boiling within 0·5°; and it was found that an ester of this purity gave a good yield of acetoacetic ester.

160. "Solubility of lead sulphate in concentrated solutions of ammonium acetate (Preliminary note)." By John Jacob Fox.

Solubility experiments were carried out with the view of determining the course of the reaction occurring between ammonium acetate and lead sulphate. The solid phases were examined to ascertain whether they changed during the solution. The following are some of the results obtained from the analysis of the solutions saturated at 24·9°, the concentration of the ammonium acetate varying from about normal upwards:

Density of solution.	Molecules of salt per 1000 molecules of water. Ammonium acetate.	Ammonium sulphate.	Lead acetate.
1·0197	20·0	0·54	0·52
1·0320	31·2	0·93	0·92
1·0457	44·5	1·49	1·46
1·0578	55·6	2·11	2·08
1·0694	68·5	2·77	2·74
1·1094	94·1	2·77	6·31
1·1281	133·3	2·80	8·10

The curve obtained does not agree with the formula developed by Noyes (*Amer. Chem. Soc.*, 1905, **27**, 747), the solubility being greater than that given by the formula. The solid phase consisted of lead sulphate and was unaltered with concentrations of ammonium acetate up to rather more than $3N$, but with more concentrated ammonium acetate, well-defined crystals of lead ammonium sulphate,

$$Pb(NH_4)_2(SO_4)_2,$$

were obtained.

The solubility of the lead sulphate increased considerably with ammonium acetate of greater concentrations than above, and the solid phases consisted of mixtures of lead sulphate and lead ammonium sulphate. The lead is probably present in solution as lead acetate, since the amount of sulphate in solution gradually became less than the equivalent of the lead present as the concentration of the ammonium acetate was increased beyond $3N$.

161. "Researches on morphine." Part III.

By Frederic Herbert Lees.

In continuation of previous work (Schryver and Lees, *Trans.*, 1900, **77**, 1024; 1901, **79**, 563, and Lees and Tutin, *Proc.*, 1906, **22**, 253), the author has shown that chloromorphide and bromomorphide yield chlorocodeide and bromocodeide respectively on methylation, the two latter bases previously obtained by other methods being simply the codeine analogues of the two former bases.

By the hydrolysis of chloromorphide, the author has isolated, besides *β-iso*morphine, an hitherto undescribed isomeride of morphine previously indicated by the hydrochloride ($[\alpha]_D$ −92·5°) obtained by Schryver and Lees. On methylation, this new base gives the so-called "*ψ*-codeine" (compare Merck, *Arch. Pharm*, 1891, **229**, 161; Vongerichten, *Ber.*, 1903, **36**, 1591, and Knorr and Hörlein, *Ber.*, 1906, **39**, 4409).

As the name *ψ*-morphine belongs to a well known oxidation product of morphine of which Merck's "*ψ*-codeine" is not the methyl ether or codeine analogue, the author has termed the new isomeride of morphine, *neo*iso*morphine* and its methyl ether, *neo*iso*codeine*.

*Neo*isomorphine, $C_{17}H_{19}O_3N$, crystallises from alcohol in brilliant, prismatic needles containing one molecule of the solvent (m. p. 278°); its *hydrochloride*, $C_{17}H_{19}O_3N,HCl$, forms anhydrous crystals from alcohol ($[\alpha]_D$ −79·1° in water); its *methiodide*, $C_{17}H_{19}O_3N,MeI$, forms glistening crystals from alcohol (m. p. 297°; $[\alpha]_D$ −54·5° in water).

*Neo*isocodeine, $C_{18}H_{21}O_3N$, forms large colourless prisms from ethyl acetate (m. p. 181—182°; $[\alpha]_D$ −96·6° in alcohol).

*β-iso*Morphine on methylation furnishes *β*-iso*codeine*, $C_{18}H_{21}O_3N$, which did not crystallise. The *methiodide*, $C_{18}H_{21}O_3N,MeI$, forms tabular crystals from water (m. p. 215—216°; $[\alpha]_D$ −145·5° in water), and on boiling with sodium hydroxide readily yields a methine base.

It was also shown that the "*A-Base*" (m. p. 147—147·5°; $[\alpha]_D$ −205·5° in chloroform) previously obtained by Lees and Tutin (*loc. cit.*) together with *iso*codeine (m. p. 171—172°; $[\alpha]_D$ −155° in chloroform) by the hydrolysis of bromocodeide as a definite substance, not resolvable by recrystallisation, is in reality a molecular combination of *iso*codeine and *β-iso*codeine.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

British Guiana. Report of the Commission appointed to enquire into and report upon the general and infantile mortality; together with minutes of the sittings, evidence of witnesses, &c. pp. viii + 154. Georgetown, Demerara. 1906. (*Recd.* 1/7/7.)

From His Excellency the Governor of the Colony of British Guiana.

Geneva, *University of.* Séance solennelle de distribution des prix de Concours, 28 Janvier, 1907. Rapports du Recteur et des Jurys précédés d'une notice biographique sur Humphry Davy [par Philippe A. Guye]. pp. 96. Genève 1907. (*Recd.* 10/6/6.)

From Professor Philippe A. Guye.

Neumann, *Bernhard.* Elektrometallurgie des Eisens. pp. x + 176. ill. Hall a S. 1907. (*Recd.* 21/6/7.) From Dr. F. M. Perkin.

Zeitschrift für anorganische Chemie. Edited by *G.* **Krüss.** Vol. I. Hamburg 1892. (*Recd.* 26/6/7.) From Professor J. W. Mallet.

THE LIBRARY.

The Library will be closed throughout the month of August, when the Society's Rooms will be redecorated, and the annual revision of the volumes will take place.

Fellows are particularly requested to return all Library Books in their possession *not later than Wednesday, July* 31*st.*

LIST OF FELLOWS, 1907.

The List of Fellows for 1907 is now in active preparation, and changes of address *received after* 31*st July cannot be included in it.*

In order that the new list may be as complete as possible, those Fellows whose degrees and Christian names do not appear in full are requested to communicate them to the Assistant Secretary.

CORRECTION.

1907. Page 144, lines 1 and 2 from top: Dr. Divers finds himself to have been in error when he assumed that Messrs. Barlow and Pope had allowed no valency to the oxygen in hydroxyl. He had read literally their expression 2Mg(F)(OH) (*Trans.*, 1906, **89**, 1686), instead of as 2Mg with 1F and 1(OH), as was intended by the authors it should be read.

The next Ordinary Meeting will be held on **Thursday**, October **24th**, **1907**, at **8·30** p.m.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK

Issued 4/11/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 330.

The following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*.

162. "Studies in the barbituric aci series. I. : 3-Diphenylbarbituric acid and some c oured derivatives." By Martha Annie Whiteley. (Trans., 1907, 1330.)

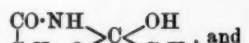
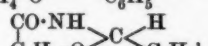
In addition to the coloured derivatives of 1 : 3-diphenylbarbituric acid already described (*Proc.*, 1906, **22**, 200; 1907, **23**, 180), 1 : 3-*diphenyl-5-diphenylmethylenebarbituric acid*, $CO<^{NPh\cdot CO}_{NPh\cdot CO}>C{:}CPh_2$, was prepared from 1 : 3-diphenylbarbituric acid and benzophenone dichloride; it forms yellow prisms melting at 264°, and, like the similarly constituted benzylidene derivative, yields a colourless acid, 1 : 3-*diphenyl-5-diphenylmethylbarbituric acid*,

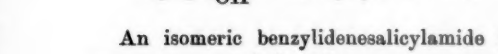
$$CO<^{NPh\cdot CO}_{NPh\cdot CO}>CH\cdot CHPh_2,$$

m. p. 205—206°, on reduction.

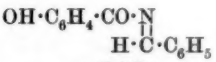
163. "Phenylbenzometoxazone and related derivatives." By Arthur Walsh Titherley. (Trans., 1907, 1419.)

According to McConnan and Titherley (*Trans.*, 1906, **89**, 1318), *O*- and *N*-acylsalicylamides are labile and mutually transformable through an intermediate cyclic metoxazone structure. The alternative tauto-

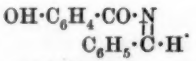
meric formula for *N*-benzoylsalicylamide is  , and the related compound, phenylbenzometoxazone,  , has been isolated by the condensation of salicylamide and benzaldehyde by means of alcoholic hydrogen chloride (compare Keane and Nicholls, *Trans.*, 1907, **91**, 266). The relation between phenylbenzometoxazone and *N*-benzoylsalicylamide is confirmed by the fact that the former passes into the latter on careful oxidation. When salicylamide and benzaldehyde condense in presence of anhydrous sodium acetate, benzylidenesalicylamide results as well as phenylbenzometoxazone :



An isomeric benzylidenesalicylamide has also been obtained by rearrangement of phenylbenzometoxazone with pyridine and alkali. The two isomerides are amorphous and similar in physical properties, but differ markedly in stability ; that produced by condensation is stable, but the other, derived from phenylbenzometazone, rearranges completely into this compound on melting. The two benzylidenesalicylamides are probably geometrical isomerides :

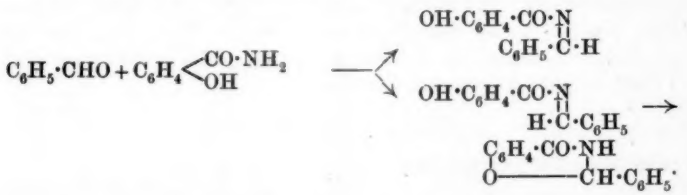


syn- (Labile) Benzylidenesalicylamide.



anti- (Stable) Benzylidenesalicylamide.

The production of phenylbenzometoxazone in the condensation of benzaldehyde and salicylamide evidently takes place through the rearrangement of *syn*-benzylidenesalicylamide first formed, so that the mechanism in presence of sodium acetate may be represented :



The reversible relation which exists between the *syn*-open-chain formula and the ring (metoxazone) affords striking confirmation of McConnan and Titherley's theory (*loc. cit.*) of cyclic metoxazone tautomerism as applied to the acylsalicylamide group.

Amorphous syn-*benzylidenesalicylamide* on boiling with alcohol or acetic acid becomes crystalline and then melts at 182°. In acetone

solution, it gives a violet ferric chloride reaction. anti-*Benzylidenesalicylamide*, which has not been obtained crystalline, gives a similar reaction. Both yield *sodium* salts and *benzoyl* derivatives.

164. "The application of Baeyer's reduction to benzoin and its derivatives." By James Colquhoun Irvine and John Weir. (Trans., 1907, 1384.)

Baeyer's method of reduction has been applied to benzoin and to a number of its derivatives. In every case, stilbene was obtained as the final product, irrespective of the nature of the side-chains present in the compound reduced. As in previous reductions of a similar nature, it has been shown that the reactions proceeded through the intermediate formation of deoxybenzoin. The reduction of benzoin to either stilbene or deoxybenzoin can be so readily controlled that the process can be used as a method of preparing these compounds, the yield being in each case about 60 per cent. of the theoretical amount.

In preparing benzoin methyl ether by Fischer's process (*Ber.*, 1893, **26**, 2412), two compounds were isolated which appear to be products of complicated side-reactions. One of these substances, which melted at 185°, is a condensation compound produced by the union of a molecule of benzoin with one of benzoin methyl ether with loss of water. The other compound (m. p. 285°) is regarded as a tetramethylene derivative produced by the union of two molecules of benzoin methyl ether. The mode of its formation resembles that of the benzoin condensation, and seems to depend on the action of nitriles present as impurities in the benzoin used.

165. "Aromatic azoimides. Part II. Ortho- and meta-hydroxyphenylazoimides." By Martin Onslow Forster and Hans Eduard Fierz. (Trans., 1907, 1350.)

o-Hydroxyphenylazoimide, $HO \cdot C_6H_4 \cdot N_3$, prepared by the action of hydroxylamine on diazotised *o*-aminophenol, crystallises in colourless needles containing $\frac{1}{2}H_2O$; it quickly becomes brown when exposed to light, darkens at 120—130°, and detonates vigorously at 140—145°. The *sodium* derivative is colourless, and does not change into a blue variety corresponding to the blue potassium derivative of *p*-hydroxyphenylazoimide. The *benzoyl*, *p-nitrobenzoyl*, and *p-toluenesulphonic* derivatives melt at 45°, 101°, and 72° respectively.

m-Hydroxyphenylazoimide, produced from diazotised *m*-aminophenol and either hydroxylamine or hydrazoic acid, crystallises from petroleum

in colourless needles which melt at 36·5° and quickly become brown when exposed to light; the *benzoyl* and *p-nitrobenzoyl* derivatives melt at 50° and 136° respectively.

166. "The influence of mercuric iodide on the formation of sulphonium iodides." By Thomas Percy Hilditch and Samuel Smiles. (Trans., 1907, 1394.)

Many sulphonium bases are difficult to obtain by the usual method namely, the addition of alkyl halide to sulphide, owing to the secondary action of the alkyl halide with the sulphonium salt as the latter is formed, and the authors have shown that ethyl disulphide and ethyl iodide, at the ordinary temperature, furnish triethylsulphonium iodide. Such instances as this are usually found where the initial addition of alkyl iodide proceeds slowly. The formation of sulphonium bases, however, is greatly accelerated if the reaction is carried out in presence of mercuric iodide; and in this way, the sulphonium salt can be isolated before the secondary action of the alkyl halide has set in. Thus ethyl disulphide and ethyl iodide in presence of mercuric iodide yield diethylthioethylsulphonium, $(C_2H_5)_3S_2I,2HgI_2$, and dibenzyl sulphide with methyl or ethyl iodide and mercuric iodide furnishes the compounds $(C_7H_7)_2(CH_3)SI,HgI_2$ and $(C_7H_7)_2(C_2H_5)SI,HgI_2$.

167. "Benzoflavol (2 : 8-dihydroxy-5-phenyl-3 : 7-dimethylacridine)." By Albert Ernest Dunstan and Louisa Cleaverley. (Trans., 1907, 1619.)

Following the method laid down by Dunstan and Hewitt (*Trans.*, 1906, **89**, 1472), the authors have prepared 2 : 8-*dihydroxy-5-phenyl-3 : 7-dimethylacridine* (*benzoflavol*) from benzoflavine. The *sulphate*, *dichromate*, *platinichloride*, and *picrate* were described.

On benzoylation, benzoflavol yields a *dibenzoyl* derivative, and on acetylation a *diacetyl* derivative, m. p. 239—242°. The latter, on methylation and subsequent hydrolysis, furnishes the *anhydro-base*, $HO\cdot C_6H_2Me\langle^{NMe}_{CPh}\rangle C_6H_2Me{:}O$.

168. "The action of bromine on 5-phenylacridine and its halogen derivatives." By Albert Ernest Dunstan and Thomas Percy Hilditch. (Trans., 1907, 1659.)

The following compounds have been prepared and submitted to the action of bromine: (1) 5-*p*-chlorophenylacridine; (2) 5-*p*-bromo-

phenylacridine; (3) 5-phenylacridine; (4) monobromophenylacridine. The resulting compounds have been methylated either by methyl iodide or dimethyl sulphate. Substances (1) and (2) gave dibromo-derivatives which lost bromine on treatment with dimethyl sulphate. Substance (3) gave a tribromophenylacridine which, with dimethyl sulphate, also lost bromine. Substance (4) was normally methylated. The authors conclude that these bromine derivatives are additive (compare Senier and Austin, *Trans.*, 1904, **85**, 1196), the added atoms occupying the para-meso-positions.

169. "The relation between viscosity and chemical constitution. Part I. The viscosity of pyridine solutions." By Albert Ernest Dunstan, Ferdinand Bernard Theodore Thole, and John Samuel Hunt. (Trans., 1907, 1728.)

The authors have applied the methods and results of Dunstan (*Trans.*, 1904, **85**, 817; 1905, **87**, 11; 1907, **91**, 83) to solutions of pyridine, α- and β-picoline, and 2:6-lutidine in various solvents. These bases in aqueous solution give curves which exhibit maxima, the discontinuities being at points of simple molecular concentration. These maxima are attributed to the addition of the elements of water at the nitrogen atom of the pyridine, or its homologues.

170. "The atomic volumes of phosphorus." By Edmund Brydges Rudhall Prideaux. (Trans., 1907, 1711.)

The author has determined the coefficients of expansion of phosphorus and phosphorus pentachloride, and has calculated the values of the constants from the equations $V_t = V_o(1 + at + \beta t^2)$, expressing the expansion of phosphorus between 60° and 235°, and $V_t = V_o(1 + at)$, expressing the expansion of phosphorus pentachloride between 160° and 190°. From these equations, values are obtained for the specific volumes of phosphorus and phosphorus pentachloride at their respective boiling points.

The atomic volume of quinquevalent phosphorus can thus be compared with those of tervalent and elementary phosphorus.

171. "The action of potassium sulphite on potassium tetrathionate in aqueous solution." By Arthur Colefax.

By the joint estimation of the iodine titration and the acidity developed in the solution when the iodine titration is completed, the

nature of the interaction of potassium sulphite and tetrathionate in aqueous solution has been investigated.

If potassium sulphite and tetrathionate react in equimolecular proportions in aqueous solution, the conversion of sulphite into thiosulphate and consequent formation of trithionate which occurs does not proceed to completion, and pentathionate is not permanently formed in the solution. If the relative proportions in which these bodies are originally present in the solution are either $K_2SO_3 : \frac{1}{2}K_2S_4O_6$, or $K_2SO_3 : 2K_2S_4O_6$, the theoretically complete conversion of sulphite into thiosulphate takes place. In the latter case, where the proportions are $K_2SO_3 : 2K_2S_4O_6$ when the sulphite has been completely converted into thiosulphate, pentathionate is found in the solution in considerable amount.

Certain preliminary experiments established that (*a*) potassium sulphite and trithionate do not react in aqueous solution; (*b*) potassium thiosulphate and tetrathionate react in aqueous solution to form pentathionate, the resulting sulphite being immediately reconverted into thiosulphate; (*c*) potassium thiosulphate and trithionate react in aqueous solution, although to an extremely small extent, and (*d*) potassium sulphite rapidly abstracts sulphur from pentathionate when the two salts react in aqueous solution.

172. "The adsorption of iodine by carbon." By Oliver Charles Minty Davis. (Trans., 1907, 1666.)

An investigation has been carried out on the adsorption of iodine, dissolved in various organic solvents, by means of animal, sugar, and cocoanut charcoal.

The main objects of the research were to investigate the effect of temperature and time on the amount of adsorption, and to compare the adsorbing values of the three forms of carbon.

The effect of temperature was found to be very small, but that of time was well marked.

The experiments demonstrate the fact that adsorption, although rapid at first, proceeds slowly for lengthened periods after a "surface equilibrium" has been maintained, proving that both surface action and diffusion are concerned in the mechanism of adsorption.

The adsorbing values of animal and sugar carbon are roughly the same, whilst that of cocoanut carbon is much less than these.

173. "Adsorption formulæ." By James William McBain. (Trans., 1907, 1683.)

The results of recent work on adsorption have been expressed by either of the following two formulæ, which are applicable to gases or solutions:

$$\text{I.}\quad \frac{x}{m} = \beta c^{1/p} = \beta\left(\frac{a-x}{v}\right)^{1/p}$$

$$\text{II.}\quad \lambda = \frac{v}{m} ln \frac{a}{a-x} = a\left(\frac{a}{v}\right)^{-1/n},$$

where x is the amount of substance adsorbed, a is the total amount of that substance, $\frac{a-x}{v} = c$ its concentration in the fluid phase, m the weight of adsorbing substance, and λ, β, a, p, and n are constants.

There are, however, some very serious disadvantages inherent in the use of the λ-formula, whereby an equilibrium is referred to a parameter a/v with which it has no apparent connexion. This expression, introduced to represent the amount of adsorption, does not lead to any definite number characteristic of each set of substances, and, moreover, its results are irreconcilable with each other and with experiment.

174. "The diazo-derivatives of benzenesulphonylbenzidine." By Gilbert T. Morgan and James Morton Hird. (Trans., 1907, 1505.)

Benzenesulphonylbenzidine and a*s-benzenesulphonylmethylbenzidine*, $C_6H_5{\cdot}SO_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, give rise to stable, coloured diazonium salts; those derived from the latter base are of interest in connexion with the formulæ recently put forward for diazonium derivatives, because they show that the presence of a labile hydrogen atom is not necessary for the development of colour in this series of substances.

175. "The interactions of aromatic amines and para-diazoimides." By Gilbert T. Morgan and Frances M G. Micklethwait. (Trans., 1907, 1512.)

The para-diazoimides recently described by the authors combine additively with the more reactive aromatic amines to give rise to aminoazo-compounds.

This combination occurs in some instances when the reagent are intimately mixed in the dry state, the reaction being accelerated by

the addition of a small amount of pyridine. Benzenesulphonyl-*p*-phenylenediazoimide combines in this way with α- and β-naphthylamines and certain of their derivatives, but the reaction does not take place with aniline and its homologues.

176. "Molecular aggregation in solution as exemplified in aqueous mixtures of sulphuric acid with inorganic sulphates." By John Holmes and Philip John Sageman. (Trans., 1907, 1606.)

The authors have determined the volumetric data of a series of mixtures of dilute sulphuric acid with aqueous solutions of neutral inorganic sulphates. In all cases, the volume of the mixture was found to be greater than the sum of the initial volumes.

From a consideration of the results obtained, the authors conclude that the volumetric changes are due to physical forces inherent to the molecules, and this theory is supported by a comparison with the results obtained in mixtures in which chemical change is known to occur.

By elimination of extraneous influences due to the solution medium, the relative aggregations of the interacting molecules can be determined.

177. "The wandering of bromine in the chlorination of bromoanilines." By Walter William Reed and Kennedy Joseph Previté Orton. (Trans., 1907, 1543.)

When *p*-bromoaniline is directly chlorinated, the normal product, 2 : 6-dichloro-4-bromoaniline, is not alone formed. Partial displacement of the bromine by the chlorine takes place, and a mixture of chlorodibromo-, dichlorobromo-, and *s*-trichloro-anilines results, which cannot be resolved into its constituents. Such a reaction does not occur only when excess of chlorine is used, but also with the calculated quantity of the reagent. The solvent has little effect, the same mixture being obtained when 20 per cent. hydrochloric acid or such anhydrous solvents as benzene, chloroform, or carbon tetrachloride are employed. Similar results were observed on treatment of 2 : 4-dibromoaniline with one molecular proportion of chlorine, *s*-tribromoaniline being among the products of the change. *o*-Bromo-, *m*-bromo-, and 2 : 6-dibromo-aniline, on the other hand, yield respectively only a single chlorinated product.

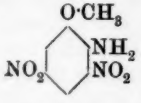
2 : 6-Dichlorobromoaniline can be obtained indirectly by two methods, either by molecular rearrangement of acetylchloroamino-2-

chloro-4-bromobenzene which yields the acetyl derivative of the aniline, or by the action of acetylchloroamino-2 : 4-dichlorobenzene on *p*-bromoaniline, when 2 : 4-dichloroacetanilide and 2 : 6-dichloro-4-bromoaniline are formed :

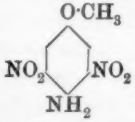
$$C_6H_4Br\cdot NH_2 + 2C_6H_3Cl_2\cdot NClAc = C_6H_2Cl_2Br\cdot NH_2 + 2C_6H_3Cl_2\cdot NHAc.$$

178. "**The diazotisation of dinitroanisidines and related compounds.**" **By Raphael Meldola and James Gordon Hay.** (Trans., 1907, 1474.)

As the result of former researches, the conclusion has been reached that the configuration essential for the displacement of a nitro-group on diazotisation is that the mobile group must not only be in the ortho- or para-position with respect to the amino-group, but that there must also be another nitro-group or acid substituent in a position adjacent to the mobile group. When these conditions are not fulfilled and the methoxy-group is in the ortho- or para-position with respect to the amino-group with a nitro-group adjacent, then on diazotisation a diazo-oxide (quinonediazide) is formed with the elimination of the methyl(methoxy) group. Two instances of this type of "diazo-reaction" have been studied, and in confirmation of the general conclusions the authors have found that the two dinitro-anisidines,



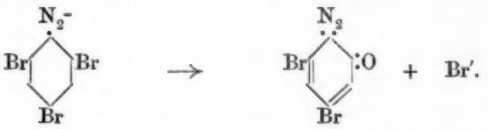
and



in which neither of the two sets of conditions above indicated is fulfilled, behave normally on diazotisation, losing neither nitro- nor methoxy-group. In the course of the present research, the authors have prepared 2 : 3-dinitro-4-aminophenol, the *N-acetyl* derivative of which crystallises in yellow needles melting at 199·5°. The free base is unstable and could not be isolated. A comparative study of the products of diazotisation of this and the corresponding dinitro-*p*-anisidine has brought out very clearly the "loosening" influence of the methyl group on the nitro-group, since under conditions in which the dinitroanisidine loses a nitro-group on diazotisation the dinitro-aminophenol retains both nitro-groups. The 2 : 3 : 5-*trinitroaminophenol*, of which the acetyl derivative was described in a paper recently published by one of the authors (*Trans.*, 1906, **89**, 1935), has also been isolated, and the products of its diazotisation studied in a preliminary way.

179. "Isomeric change in benzene derivatives. Replacement of halogen by hydroxyl in chlorobromodiazobenzenes." By Kennedy Joseph Previté Orton and Walter William Reed. (Trans., 1907, 1554.)

In continuation of earlier work (Orton, *Proc. Roy. Soc.*, 1902, **71**, 153; Proc., 1902, **18**, 252; *Trans.*, 1903, **86**, 796; *ibid.*, 1905, **87**, 99) on the transformations of halogendiazobenzenes, in which an atom of halogen is replaced by hydroxyl, a quinonediazide resulting, thus:



a study has now been made of mixed symmetrical chlorobromodiazobenzenes. For this purpose, the diazo-compounds which are obtainable from 2 : 6-dichloro-4-bromo-, 2 : 4-dichloro-6-bromo-, 4-chloro-2 : 6-dibromo-, and 6-chloro-2 : 4-dibromo-anilines have been used. *3-Chloro-5-bromo-p-toluidine* (which has not been hitherto described) was also prepared for the same purpose.

From these experiments, which were carried out in the manner followed previously, two facts have been elucidated. The replacement of halogen by hydroxyl is not exclusively confined to the halogen atoms which are in the ortho-position with respect to the diazo group. Some 20 per cent. of the molecules of the diazo-compound lose an atom of halogen from the para-position, a *p* quinonediazide being formed.

When all other conditions are alike (such as relative positions in the benzene ring, contiguity of other substituting groups, &c.), the displacement of the halogen appears to be independent of the nature of the halogen. Thus 80 per cent. of the molecules of 2 : 6-dichloro-4-bromodiazobenzene and 4-chloro-2 : 6-dibromodiazobenzene respectively lose one atom of chlorine or bromine from the ortho-position; again, 50 per cent. of the molecules of 3-chloro-5-bromo-*p*-diazotoluene lose an atom of chlorine from one ortho-position (with respect to the diazo group) and 50 per cent. lose bromine from the other ortho-position.

The authors consider that the position to which the hydroxyl becomes attached will depend rather on the general symmetry and configuration than on the nature of the halogen atom occupying the given position.

180. "A new colouring matter from Nyctanthes Arbor-tristis." **B Ernest George Hill and Annoda Prasad Sirkar.** (Trans., 1907, 1501.)

The flowers of *Nyctanthes Arbor-tristis* yield a yellow dye soluble in water. On heating the aqueous extract in dilute hydrochloric acid, a reddish-brown, flocculent precipitate is formed. The greater part of this is soluble in alcohol, but cannot be crystallised from this solvent. If the alcoholic solution is gently warmed with a few drops of concentrated hydrochloric acid, a bright red sediment forms and the solution loses most of its colour. This substance crystallises from pyridine or phenylhydrazine and has the formula $C_{20}H_{27}O_4$. It is slightly acid, very sparingly soluble in most solvents, but readily in alkalis. It forms the *acetyl* compound $C_{20}H_{26}O_3 \cdot C_2H_3O$, but contains no methoxyl groups. It gives neither phloroglucinol nor pyrocatechol on fusion with potassium hydroxide.

The flocculent precipitate gives a bromine compound, $C_{20}H_{15}O_{18}Br_5$, which yields bromoform on warming with potassium hydroxide.

The name *nyctanthin* is suggested for the red, crystalline substance $C_{20}H_{27}O_4$.

181 "The velocity and mechanism of the reaction between iodine and hypophosphorous acid." **By Bertram Dillon Steele.** (Trans., 1907, 1641.)

The velocity and mechanism of the reaction between iodine and hypophosphorous acid have been investigated under various conditions.

It has been found that the velocity of the reaction is independent of the concentration of the iodine provided this does not fall below a certain limiting value. This behaviour is best explained by the supposed occurrence of consecutive reactions of such a nature that the iodine takes no part in the slower or controlling reaction.

The reaction is unimolecular with respect to the hypophosphorous acid and it is catalytically accelerated by hydrogen ions, the velocity under certain conditions being directly proportional to the concentration of the latter.

Since hydrogen ions are formed during the course of the reaction, the latter becomes autocatalytically accelerated in the absence of any large initial concentration of acid.

The further oxidation of phosphorous acid to phosphoric acid by iodine is one which is retarded by the presence of hydrogen ions. It should furnish therefore an example of autocatalytic retardation.

182. "Succinic acid and its potassium salts." By Hugh Marshall and Alexander Thomas Cameron. (Trans., 1907, 1519.)

In a previous paper (*Proc. Roy. Soc. Edin.*, 1905, **25**, 401), Cameron described the preparation of crystals of acid potassium succinate showing curved faces. The authors have now continued that research, giving further particulars of these curved crystals, and, more particularly, a description of the pure potassium salts themselves, since trustworthy data concerning these have not hitherto been published. The conditions of equilibrium for aqueous solutions containing potassium and hydrogen succinates were studied at various temperatures. At the ordinary temperature, solutions having the composition of the superacid salt, $KH_3(C_4H_4O_4)_2$, first deposit succinic acid; solutions having the composition of the acid salt, $KHC_4H_4O_4$, first deposit the superacid salt. Above 30—35°, however, the acid salt is in equilibrium with a solution having a similar composition, and it would also appear that at a considerably higher temperature the same is true for the superacid salt.

It seems probable from the results obtained that the superacid salt is not merely a "molecular" compound, but that the complex ion $H_3C_4H_4O_4'$ exists in considerable proportion in the solution, especially at higher temperatures.

The acid salts, $KHC_4H_4O_4$, $KHC_4H_4O_4.2H_2O$, and $KH_3(C_4H_4O_4)_2$, were examined crystallographically; these, with the normal salt, $K_2C_4H_4O_4,2H_2O$, were the only potassium salts of succinic acid obtained within the limits of temperature covered by the investigation.

183. "The fluoresceins and eosins from 4-hydroxyphthalic, 4-methoxyphthalic, and hemipinic acids." By Arthur Friedl, Charles Weizmann, and Max Wyler. (Trans., 1907, 1584.)

Resorcinol condenses readily with 4-hydroxyphthalic, 4-methoxyphthalic, and hemipinic acids, yielding the corresponding *hydroxy-*, *methoxy-*, and *dimethoxy-fluoresceins*. Hydroxyfluorescein is very slightly fluorescent, whereas methoxyfluorescein, like ordinary fluorescein, is extremely so. Dimethoxyfluorescein is much less fluorescent than is methoxyfluorescein.

The corresponding tetrabromo-derivatives of these fluoresceins show corresponding differences in their fluorescent properties.

184. **"Researches on anthraquinones and phthaleins."** By **William Henry Bentley, Henry Dent Gardner, jun., and Charles Weizmann.** (Trans., 1907, 1626.)

Hydroxymethylanthraquinones can be prepared in two stages from phthalic acid (or its derivatives) and the cresols (or their methyl ethers). A derivative of benzoylbenzoic acid is first prepared and subsequently condensed by sulphuric acid to the corresponding hydroxymethylanthraquinone:

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3Me\cdot OH \longrightarrow C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_2Me\cdot OH.$$

The authors have employed two condensing agents for bringing about the first reaction, namely, (1) boric acid and (2) aluminium chloride, obtaining different results in each case where this was possible. Boric acid promotes condensation in the ortho-position, whereas aluminium chloride causes condensation to take place in the para-position with respect to the hydroxyl group.

A number of condensations of phthalic and hydroxyphthalic acids with the three cresols and *m*-4-xylenol have been effected.

185. **"Derivatives of naphthacenequinone. Part II."** By **William Henry Bentley, Arthur Friedl, and Charles Weizmann** (Trans., 1907, 1588.)

The two nitrophthalic acids condense with α-naphthol, yielding nitrohydroxynaphthoylbenzoic acids,

$$NO_2\cdot C_6H_3(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH,$$

which on reduction yield the corresponding amino-acids; the latter condense in sulphuric acid to aminohydroxynaphthacenequinones, which thus contain the amino-group in the benzene ring:

$$NH_2\cdot C_6H_3\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_{10}H_5\cdot OH.$$

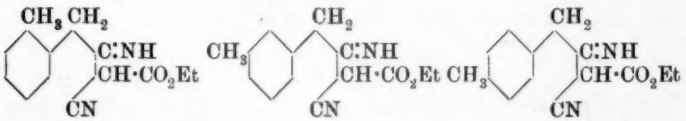
These derivatives dissolve in concentrated sulphuric acid with a much bluer, and in alcoholic potash with a much yellower, colour than is exhibited by 1-amino-6-hydroxynaphthacenequinone, which contains the amino-group in the naphthalene ring.

Hemipinic acid condenses with α-naphthol, yielding *hydroxydimethoxynaphthoylbenzoic acid*, $(CH_3\cdot O)_2C_6H_2(CO_2H)\cdot CO\cdot C_{10}H_6\cdot OH$, which when heated with sulphuric acid appears to hydrolyse and also oxidise during the condensation, the product on analysis giving numbers corresponding with *trihydroxymonomethoxynaphthacenequinone.*

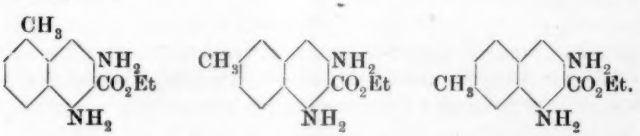
1 : 5-Dihydroxynaphthalene, being a di-α-naphthol, can condense with two molecules of phthalic acid, yielding *dicarboxybenzoyldihydroxynaphthalene*, $CO_2H \cdot C_6H_4 \cdot CO \cdot C_{10}H_4(OH)_2 \cdot CO \cdot C_6H_4 \cdot CO_2H$. This acid, however, on condensation with sulphuric acid appears to lose one phthalic acid group, yielding a *trihydroxynaphthacenequinone*.

186. "The formation and reactions of imino-compounds. Part V. The formation of methyl derivatives of 1 : 3-naphthylenediamine from the three tolylacetonitriles." By Ernest Francis Joseph Atkinson and Jocelyn Field Thorpe. (Trans., 1907, 1687.)

In order to throw some light on the colour change which ensues when ethyl β-imino-α-cyano-γ-phenylbutyrate is transformed into the sulphate of ethyl 1 : 3-naphthylenediamine-2-carboxylate by the action of concentrated sulphuric acid, the three methyl derivatives of this ethyl salt, containing the methyl group in the benzene nucleus, have been prepared and investigated. These three isomeric forms of ethyl β-imino-α-cyano-γ-tolylbutyrate :



pass on treatment with cold concentrated sulphuric acid into the corresponding methyl derivatives of ethyl 1 : 3-naphthylenediamine-2-carboxylate :



These ethyl salts on hydrolysis yield the corresponding carboxylic acids, which readily evolve carbon dioxide and pass into 1-methyl-5 : 7-naphthylenediamine, 2-methyl-5 : 7-naphthylenediamine, and 2-methyl-6 : 8-naphthylenediamine respectively.

Whereas the transformation of the meta-compound into the naphthalene ring at −5° is, like the other cases investigated previously, practically quantitative, the yield of the naphthalene derivative from the ortho- and para-compounds is scarcely 10 per cent. of the theoretical, the main product of each reaction being a phenolic base which is characterised by giving an intense colour with concentrated sulphuric acid.

The malachite-green solutions which were formed at the ordinary temperature, but not at $-5°$ in the reactions previously investigated, are therefore probably due to the formation of similar phenolic bases, since the naphthalene derivatives formed in the reactions do not themselves give colours with sulphuric acid. The following are the colour reactions of the three isomeric ethyl salts named towards concentrated sulphuric acid at the ordinary temperature.

Ethyl β-imino-α-cyano-γ-*o*-tolylbutyrate dissolves, forming an intense red-brown solution, which on dilution becomes first olive-green and finally yellow.

Ethyl β-imino-α-cyano-γ-*m*-tolylbutyrate forms a cherry-red solution, which becomes colourless on dilution.

Ethyl β-imino-α-cyano-γ-*p*-tolylbutyrate dissolves, forming an intense magenta-red solution, which on dilution becomes first violet, then blue, then green, and finally yellow.

No colour is formed in the case of the meta-derivative at $-5°$, but lowering of the temperature has no effect on the colour formation of the ortho- and para-compounds.

187. "The chemical action of radium emanation. Part II. On solutions containing copper and lead, and on water." By Alexander Thomas Cameron and Sir William Ramsay, K.C.B. (Trans., 1907, 1593.)

Radium emanation, as is known, yields helium when allowed to stand alone or mixed with oxygen and hydrogen gases. When dissolved in water, the gaseous product is neon, containing a trace of helium, and in presence of copper nitrate, the product is argon, containing no recognisable trace of helium. The copper solution, after the emanation has decayed in contact with it, is found to contain a trace of lithium; at the same time, the weight of the residue, which consists mainly of sodium salts, is considerably increased. The experiments were carried out in glass bulbs.

The authors suggest as a hypothesis: (1) that helium and the α-particle are not identical; (2) that helium results from the "degradation" of the large molecule of emanation by its bombardment with α-particles; (3) that this "degradation," when the emanation is alone or mixed with oxygen and hydrogen, results in the lowest member of the series to which the emanation undoubtedly belongs, namely, helium; (4) that if particles of greater mass than hydrogen or oxygen are associated with the emanation, namely, liquid water, then the "degradation" is less complete, and neon is produced; (5) that when molecules of still greater weight and complexity are present, as is the case when the emanation is dissolved in a solution of a copper

salt, the product of "degradation" of the emanation is argon. They are also inclined to believe that the copper also is involved in this process of degradation, being reduced to the lowest member of its series, namely, lithium, and they suspect that, at the same time, sodium is produced in much greater quantity than lithium. Experiments on the gases evolved from thorium nitrate show that carbon dioxide is one of the products; this might be interpreted by the same hypothesis, in supposing carbon to be formed by the degradation of thorium, the highest member of the carbon series.

188. "Indican. Part I." By Arthur George Perkin and William Popplewell Bloxam. (Trans., 1907, 1715.)

Indican, $C_{14}H_{17}O_6N,3H_2O$, crystallises from a mixture of benzene and alcohol in anhydrous prisms, m. p. 176—178°, and in this form can be readily recrystallised from absolute alcohol. On hydrolysis with dilute acids in the presence of isatin, a quantitative yield of indirubin is obtained, as predicted by Beyerinck (*Proc. K. Akad. Wetensch. Amsterdam*, 1899, **2**, 120), but a theoretical yield of indigotin has not as yet been produced from it by a combination of hydrolysis and oxidation. When indican is digested with boiling dilute acid in absence of air, a complex reaction occurs, a trace of indole being formed together with dextrose (compare Hazewinkel, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 512) and brown, amorphous substances. The main constituent of the latter, for which the name *indoxyl-brown* is suggested, has a similar composition and closely resembles the chief constituent of indigo-brown (*Trans.*, 1907, **91**, 295), with which it is, no doubt, closely allied, but, on the other hand, it is more soluble in alcohol, and differs from it in certain minor respects. It has been found possible to isolate as much as 30 grams of crystalline indican from 1 kilogram of the leaves of the *Indigofera Sumatrana*.

189. "The occurrence of quercitol (quercite) in the leaves of Chamaerops humilis." By Hugo Müller.

This paper gives a short account of the occurrence of quercitol (quercite) in the leaves of *Chamaerops humilis*, the only species of the palm family indigenous in Europe.

These leaves in the dry state yield as much as 1·35 per cent. of this substance, and, as it can be obtained from them by a very simple process, may form a suitable material for its preparation.

This quercite is the dextro-modification and is identical with that obtained from acorns.

190. "Cocositol (cocosite), a constituent of the leaves of 'Cocos nucifera' and 'Cocos plumosa.'" By Hugo Müller.

Cocosite, isomeric with inosite, is contained in the leaves of *Cocos plumosa* and *Cocos nucifera* and also in the so-called milk of the cocoanut. In general chemical character, it resembles inosite and shows the characteristic rhodizonic acid reaction, but differs very widely in its physical properties, such as crystalline form, melting point, and solubility in water.

A *hexa-acetate*, a *nitrate*, and *sulphonic acids* have been obtained and examined.

Cocosite still more closely resembles the quercenin found by Delachanel and Vincent in the acorn and also the scyllit of Staedeler and Frerichs, recently re-investigated by J. Müller. It seems highly probable that these three substances are identical.

191. "Inositol (inosite)." By Hugo Müller.

The difficulty of procuring a somewhat larger supply of material for the fuller investigation of cocosite suggested a previous study of the behaviour of the isomeric inosite, when submitted to the reactions contemplated for this purpose, as the results thus obtained would serve as a guide and indirectly effect an economy in the use of cocosite.

A considerable quantity of inosite, which had been prepared from cochineal, furnished the material for this investigation.

The behaviour of inosite hexa-acetate, when submitted to the action of a saturated solution of hydrogen bromide in glacial acetic acid in the manner described by W. H. Perkin, jun., and J. L. Simonsen, has been investigated and also the reaction of hydrogen peroxide in conjunction with ferrous sulphate on inosite according to the methods devised by Fenton.

Monobromoinosite penta-acetate, two isomeric forms of *dibromoinosite tetra-acetate*, and also *inosite dibromohydrin* have been fully examined.

On treating the monobromo-penta-acetate with zinc dust, it loses its bromine along with one molecule of acetic acid.

If, on the other hand, the dibromoinosite tetra-acetates are treated in the same manner, phenol and acetic acid are the only products.

The treatment of inosite by Fenton's method with hydrogen peroxide yields, with a transitory dark violet-blue coloration, besides

some oxalic acid, a substance which has not yet been obtained in a definite form, but from which the barium rhodizonate and potassium-croconate have been prepared.

October 18th, 1907. Extra Meeting, Sir W. RAMSAY, K.C.B., F.R.S., President, in the Chair. This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

The PRESIDENT, in opening the proceedings, said: Professor Fischer needs no introduction to you; but I may remind you that he was asked to give the Faraday Lecture in 1895. At that time his health precluded him from coming to England, and we have now to congratulate him that his health has greatly recovered, and ourselves especially on his having come among us to-night to deliver the Faraday Lecture. I shall not, however, take up any more time, but at once ask Professor Fischer to deliver his address.

Professor FISCHER, speaking in German, then delivered the Faraday Lecture, of which the following account is an abstract:*

"Synthetical chemistry in its relation to biology."

We know that in nature the construction of organic matter begins in the leaves of plants with the conversion of carbon dioxide into sugar, from which many physiologists suppose the complex substances contained in the living cell are formed by further changes in which nitrogen, sulphur, and phosphorus take part.

Nothing definite, however, is known even of the assimilation of carbon dioxide, and although it is now possible to effect the complete synthesis of sugar at temperatures such as prevail in the living plant, our laboratory methods fall far short of the efficient manner in which this work is accomplished in nature. One peculiarity of the natural change is the asymmetric character of the synthesis, and I showed some time ago that it is possible to give a fairly satisfactory explanation of this. It is only necessary to assume that the condensation is preceded by the formation of an additive compound of formaldehyde with some optically active constituent of the chlorophyll granules. I am inclined to think that this compound with carbon dioxide undergoes decomposition into oxygen and a reduction product, probably a derivative of formaldehyde; the condensation to sugar takes place either in the original asymmetric complex or in one produced

* Full report, Trans., 1907, p. 1749.

from it by a secondary change involving the separation of the formaldehyde and its re-association in some other manner.

The formation of fats in plant and animal tissue is no less complicated a phenomenon. It is certain that carbohydrates are the chief source of supply. We know next to nothing, however, of the actual course of this remarkable synthesis; it is easy to imagine that glycerol may be formed by the hydrolysis of glucose, and that three molecules of glucose may give rise to an acid containing eighteen carbon atoms. But the process involved in the conversion of sugar which is rich in oxygen into fatty acids containing little oxygen remains wrapped in mystery. I imagine that this change, like that which attends alcoholic fermentation, is effected by a rearrangement of oxygen atoms within the molecule, and that it involves the elimination of carbon dioxide.

The problems afforded by the fats are simple, however, in comparison with those connected with the carbohydrates.

Up to the present time only the monosaccharides have been studied satisfactorily from the point of view of their spatial structure. The dogma which at one time prevailed that Nature produces only carbohydrates with six atoms of carbon was upset by Kiliani's discovery that arabinose contains but five atoms of carbon. Since then the group of the monosaccharides has been so extended by synthetic means that sugars of all types are now known, the group including besides the seven compounds which occur naturally no less than forty-five synthesised products.

The growth of our knowledge of the monosaccharides has proved in many ways to be of importance in connexion with biological inquiry, especially in enabling us to penetrate the mystery of enzyme action somewhat further.

On contrasting the effects which emulsin and the enzymes in yeast produce on the various glucosides prepared by synthetic methods, I was led to conclude not only that there was a difference between the two series of optical antipodes similar to that discovered by Pasteur in the course of his studies of moulds but that very slight changes in configuration were sufficient to inhibit the action of enzymes entirely. I was led by these observations to apply the simile of *lock* and *key* as an expression of the close inter-relationship in configuration which obtains between the enzyme and the substance which it attacks.

The experience gained with the glucosides became of service in studying the polysaccharides and, as the result of my investigations, I was able to formulate a rule of general biological significance, namely, that the alcoholic fermentation of a polysaccharide is necessarily preceded by its hydrolysis by some particular enzyme. It was

shown, especially in the case of the invertase of *Monilia Candida*, that it is not essential that the enzyme should even be soluble in water.

Unfortunately but few successful syntheses of polysaccharides have been effected. Musculus obtained dextrin-like products from grape sugar by treating it with mineral acids; and I have shown that a disaccharide, *iso*maltose, may be produced in this way.

The carbohydrate group is that in which use was first made of enzymes as synthetic agents. Croft Hill has the great merit of having been the first to demonstrate the reversibility of enzyme action, and an important extension of Croft Hill's discovery is afforded by E. F. Armstrong's observation that the action of emulsin is different from that of the enzymes of yeast, the condensation of glucose taking place in such a way that a disaccharide which appears to be maltose is formed together with other complex products. Such syntheses, however, cannot take the place of purely chemical methods, as these latter are so much more under our control, and can be varied in so many ways, that we are in the position to produce materials which it is quite impossible for the organised world to furnish.

This contention is applicable to the proteins even more than it is to the carbohydrates: as they are among the most complex substances produced in the living world and are concerned in all the vital activities of the cell, a complete comprehension of their nature must obviously precede the full development of biological chemistry.

Of the numerous attempts to unravel the constitution of the proteins by analytical means, the only method which has given useful results hitherto is that of hydrolysis. Hydrolysis can be effected by acids or by alkalis and also by digestive enzymes; the products, it is well known, besides ammonia, are albumoses, peptones, and ultimately amino-acids. The complete synthesis of the active amino-acids which are obtained from natural sources was first accomplished by the method I introduced based upon the use of the acyl derivatives. The method has been applied with success to the majority of the synthetic products; its extension to the remaining cases, proline, lysine, tryptophane, and cystine, is not likely to be attended with any difficulties.

As the amino-acids are formed from the proteins, not only when these are subjected to the action of hot acids and alkalis, but also at moderate temperatures by the agency of the digestive enzymes, they are to be regarded as the true foundation stones of protein molecules and it has been found to be possible, by a process the reverse of hydrolysis, to associate amino-acids in such a manner that substances are produced which, in the case of the simpler terms, closely resemble peptones, whilst the more complex resemble proteins.

I have termed these synthetic products *polypeptides*, in view of their relationship to the peptones and to facilitate systematic treatment of

the group on the lines of the carbohydrates; more than one hundred of these artificial polypeptides have already been synthesised.

By making use of new methods based on the study of the polypeptides, it has been possible during the last two years to isolate and detect with certainty quite a number of dipeptides among the decomposition products of the proteins. In conjunction with Abderhalden, I have succeeded in separating glycyl-*d*-alanine, *d*-alanyl-*l*-leucine, and *l*-leucyl-*d*-glutamic acid from silk fibroin, elastin, and gliadin respectively. We have definitely proved the existence of dipeptides of glycine with *l*-leucine and *l*-tyrosine in the form of anhydrides, and our work has made it probable that other combinations exist, for example, that of glycine with valine.

A tetrapeptide of fairly definite composition has been isolated by Abderhalden and myself from silk fibroin and, although its homogeneity is not yet quite established, it is certainly in great part a combination derived from two glycine molecules with one of *d*-alanine and one of *l*-tyrosine. The substance is of special interest on account of its close resemblance to the albumoses. Moreover, *l*-leucyl-triglycyl-*l*-tyrosine prepared artificially has all the properties of the albumoses. These observations are of importance as casting doubt on the view which formerly prevailed that, being intermediate products between proteins and peptones, the albumoses are substances of considerable molecular complexity.

In presenting the Faraday Medal to Prof. Fischer at the conclusion of the lecture, the PRESIDENT said: Before I call on Sir Henry Roscoe, I have great pleasure, Prof. Fischer, in the name of the Chemical Society in handing over to you this medal as a testimony of our great regard for you as our foreign member and of our affection for you as a man.

Sir HENRY ROSCOE: Mr. President, Ladies and Gentlemen,—I have had the good fortune to hear many Faraday Lectures. I remember with pleasure the eloquence of Dumas; the charm of Wurtz, and the thought and beautiful diction of Helmholtz; but, Mr. President, I do not think that any of our Faraday Lectures has awakened greater interest than the one to which we have just listened; and this, not only because Prof. Emil Fischer is a master of his subject, and because he has laid before us work mainly accomplished by his own inventive brain and his own able hands, but also because the subject of the application of synthetical chemistry to biology which the lecturer has so ably brought before us is one which at the present moment is exceeded in interest and importance by no other branch of the science, not even—if I may be allowed, in the presence of the President, to say so—by that of radio-activity. Of the nature and

character of the work which Prof. Emil Fischer has accomplished, the Fellows of the Chemical Society are good judges. When some years ago we learned that Emil Fischer had synthesised the sugars, all chemists were loud in their expressions of satisfaction and admiration. How much greater will those expressions be now when we learn what success has attended the apparently almost insoluble problem of the synthesis of the proteins.

If the one resembles the ascent of some unconquered Swiss peak, the other may be compared with the far greater feat of the attempt to reach the top of Mount Everest. But even supposing the last thousand feet of the mountain have proved to be too much for the strength of the mountaineer, yet the most important result has been achieved, for the route has been laid down and the directions given by which subsequent explorers may gain the summit. As Emil Fischer has already succeeded in this synthesis of the sugars, so he has pointed out the method by which he himself, as we all hope, or others following in his footsteps, will succeed in fully unravelling the constitution of those chemical mysteries, the proteins. By this grand work he has won for himself the admiration of us all—of all those who are interested in scientific discovery; and for bringing this subject before us in so able a manner I have the honour and pleasure of proposing a vote of thanks.

Sir James Dewar: Mr. President, Ladies and Gentlemen,—I am exceedingly grateful to the Council for the honour which they have done me and more especially the Institution by asking me to second the admirable and eloquent vote of thanks which Sir Henry Roscoe has proposed. I assume that this has been conferred upon me as a tribute to the great man whom we have come here, Sir, to honour. For some thirty-four years, Faraday held the Chair, which I have had the honour of holding, I am sorry to say, for now nearly thirty years. I cannot help thinking that the last portion of your address, in particular where you deal with the aims and method of the investigator, as well as the part that has been put so prominently before us by Sir Henry Roscoe, would have specially appealed to Faraday. Sometimes we have too great brilliancy in investigation. We have been told that the foundations of our science are being shaken, that we are living in an age in which the chemistry of the past will disappear, and that we shall have to reconstruct it on an entirely new basis. Now, Sir, I think you have conferred, by your work, the greatest honour upon the chemistry of the past. You have worked along the beaten lines of scientific investigation founded by Liebig, followed by Hofmann, Wurtz, Kekulé, and Baeyer, and have shown that, by following these ancient tracks, you can now assimilate new ground in a manner which these chemists would never have believed

possible. In that way, Sir, you have consolidated the science of chemistry. However much, as Sir Henry Roscoe pointed out, we may wonder and admire radium, still we cannot but admit that the chemistry of carbon is the most extraordinary of that of all the elementary bodies, and that you, Sir, have done more than any man living to convince us of the possibility of yet further achievements in organic synthesis. What you have done would, I think, have appealed very much to Faraday, from the fact that you have worked in this magnificent, steady, undespairing, but yet successful way. There is a very admirable story of your great countryman, Luther, which represents the spirit of Faraday. Some very inquisitive person was anxious to obtain from Luther his opinion as to whether certain passages in the Scriptures were canonical or apocryphal, and Luther replied that the saints who particularly appealed to him were those of whom no marvellous stories had been recorded; who lived their lives without pretence like other people, and who did not desire to make themselves notorious. I am perfectly certain that was the mind of Faraday, and that is the mind of Emil Fischer. The man is sometimes greater than his work, and we admire you, Sir, not only for your work, but as a man. May I say that in coming here you have done a double honour to the Royal Institution. Perhaps you may be unaware of it. It has sometimes been said that the greatest discovery that Davy ever made was Faraday. You can hardly dissociate the one from the other. Now you have selected spontaneously this date for the first lecture of the season, although the Royal Institution really does not open until Christmas, and to-morrow is the centenary of the discovery of the alkali metals by Sir Humphry Davy. I do not know whether you knew this fact—but you have come here, and you have adorned both the names of Faraday and Davy by lecturing in the same room, which is practically in the same condition and at the same table where they have so often discoursed. I have to convey to you the hearty thanks of all the members of the Institution. We wish you long life to continue your great labours to adorn science, not only Germanic science, but the science of the world.

The CHAIRMAN having put the vote to the meeting, it was carried with acclamation.

Professor FISCHER, speaking in English, said: Mr. President, Ladies and Gentlemen,—I owe you my sincere thanks for the kind recognition which you have been so good as to extend to my modest endeavours. I have felt exceedingly honoured in having received this invitation of the Chemical Society to come here to deliver the Faraday Lecture, and to pay homage to the great discoverer who so often on this very spot announced the results of his wonderful

researches. But it affords me a keener pleasure to recall on this occasion the constant friendly intercourse which has existed during many generations between the English and the German men of science, and which has led to much happy exchange of scientific thought.

Thursday, October 24th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. J. V. J. Hayman, J. W. Shepherd, and C. H. Warner were formally admitted Fellows of the Society.

The PRESIDENT reminded Fellows of the loss which the Society had sustained since the previous meeting by the death of Sir William Henry Perkin, Dr. John Clark, Dr. August Dupré, and Mr. F. J. M. Page.

It was announced, also, that on the occasion of the Centenary Celebration of the Geological Society, the following address was presented:

In the name of the Chemical Society we welcome the present opportunity of offering our warmest congratulations to the President, Council, and Fellows of the Geological Society of London on the occasion of its Centenary Celebration.

It is impossible to overestimate the value of the great work which your Society has accomplished during the past hundred years, both in laying the solid foundations of a new science and in helping to raise on these foundations the stately edifice of Modern Geology.

The connexion between Geology and Chemistry has always been, and must ever remain, a very intimate one, and the early history of your Society shows that Chemists a hundred years ago fully recognised that their special branch of Natural Knowledge was destined to play an important part in elucidating those changes in the structure of the earth which fall within the special province of the Geologist.

This association between the two Societies is brought into further prominence by the fact that amongst the thirteen original founders of your Society, we find the names of no less than five celebrated chemists, viz., Arthur Aikin, William Allen, Humphry Davy, W. H. Pepys, and Richard Phillips; whilst within the first few years of your corporate existence the roll of your Fellows includes the names of Thomas Thomson, William T. Brande, Edward Turner, James Hall,

W. H. Wollaston, J. F. Daniell, Charles G. Daubeny, and Alexander J. Marcet.

The advances in Modern Petrology, a subsection of Geology which may be said to have been initiated by your Society, have demanded a still closer union between our respective branches of Science, and in the new ideas introduced within the last decade by the discovery of radio-activity we see further indications that Physical Chemistry in the near future must influence many of the fundamental doctrines bearing on the age of the earth, and on the various changes which the earth has undergone within the period embraced by Geology.

Signed, on behalf of the Chemical Society,

WILLIAM RAMSAY, *President.*
ALEXANDER SCOTT, *Treasurer.*
M. O. FORSTER, } *Honorary*
ARTHUR W. CROSSLEY, } *Secretaries.*
HORACE T. BROWN, *Foreign Secretary.*

Certificates were read for the first time in favour of Messrs.:

John Forbes Bell, Craigmillar, Edinburgh.
Edward Joseph Day, M.D., M.R.C.S., L.S.A., Dorchester, Dorset.
Frederick Harold Dupré, Mount Edgcumbe, Sutton, Surrey.
Percy Vivian Dupré, A.C.G.I., Mount Edgcumbe, Sutton, Surrey.
Francis Bridger Dutton, Birch Hall, Windlesham, Surrey.
Thomas Rigby Greenough, B.A., Beechwood, Leigh.
William Doge Hutchinson, B.A., Lythmore, Tennyson Rd., Harpenden.
Harry Ingham, M.Sc., 26, Hamilton Street, Bury.
Herbert Marsden, B.Sc., Bramford, Ipswich.
Herbert Frederick Sankey Marshall, High Street, Burwell.
Gerald Hargrave Martin, Delce, Park Road, Wallington.
John Edward Langford Moore, Walton Cottage, Loughboro' Park, S.W.
Charles Samuel Mummery, Christ's Hospital, West Horsham.
Harold Ramsay Stobie, Clovelly, Craighall Gardens, Edinburgh.
Frederick Thomas, B.Sc., 29, Fairhaven Rd., St. Annes-on-the-Sea.
Harold Munkman Timpany, M.Sc., St. Winifrede's Gardens, Shrewsbury.
George Arthur Watson, A.R.C.S.I., 7, Roseneath Villas, Cork.
Edward Wheeler, A.C.G.I., 113, Highbury Quadrant, N.
Robert Whymper, A.C.G.I., St. Clare, St. Mary's Rd., Ditton Hill.
Percy Williams, B.Sc., c/o The Wilhelmina Co., Pontianak, Dutch West Borneo.
William John Wilson, A.C.G.I., 28, Windmill Street, Gravesend.

Of the following papers, those marked * were read:—

***192. "The constitution of phenol- and quinol-phthalein salts: a contribution to the quinonoid theory of colour." By Arthur George Green and Percy Edgar King.**

Prof. Green gave an account of the following investigation which has been described in *Ber.*, 1906, **39**, 2365; 1907, **40**, 3724.

Green and A. G. Perkin have adduced evidence as to the constitution of phenol- and quinol-phthalein salts which cannot be reconciled with the indicator theory of Ostwald. On the other hand, the view that the appearance of colour during salt formation is due to a change of type from the lactone or triphenylcarbinol form to the quinonoid form has hitherto not met with general acceptance, largely owing to the failure of repeated attempts to obtain coloured carboxylic esters of these phthaleins.

The authors have now succeeded in preparing the coloured carboxylic esters, not only of the phthaleins themselves, but also of their mono- and di-methyl ethers. These esters, which are orange to red, are extremely unstable, being readily saponified, not only by weak acids or alkalis, but even by water. They form with acids, oxonium salts which are of a deeper colour than the free esters. Whilst the esters of phenolphthalein, $C_6H_4(CO_2Me)\cdot C\lessdot^{C_6H_4\cdot O}_{C_6H_4\cdot OH}$, and of monomethylphenolphthalein, $C_6H_4(CO_2Me)\cdot C\lessdot^{C_6H_4\cdot O}_{C_6H_4\cdot OMe}$, were obtained in the free state and are more stable than their chlorides, the esters of quinolphthalein and of monomethylquinolphthalein could only be isolated in the form of the oxonium salts, thus:

$$C_6H_4(CO_2Me)\cdot C\lessdot^{C_6H_3(OH)}_{C_6H_3(OH)}\gtrdot O\cdot Cl.$$

The esters of dimethylphenolphthalein and of dimethylquinolphthalein (trimethyl derivatives) are only capable of existence as salts, a fact which agrees well with the representation of the chlorides as

$$C_6H_4(CO_2Me)\cdot C\lessdot^{C_6H_4\cdot OMe}_{C_6H_4\cdot OMe}\lessdot^{H}_{Cl}$$ and

$$C_6H_4(CO_2Me)\cdot C\lessdot^{C_6H_3(OMe)}_{C_6H_3(OMe)}\gtrdot O\cdot Cl.$$

The monomethyl esters of both phthaleins are soluble in alkalis, giving strongly coloured solutions similar to those of the phthaleins themselves, but not decolorised by an excess of alkali. On the other hand, the isomeric lactone ethers are colourless and do not give coloured salts.

These facts disclose an exact parallelism between the esters and salts of these phthaleins and those of fluorescein, and place the quinonoid structure of these substances almost beyond question.

Discussion.

Dr. Hewitt remarked that in certain cases it was very difficult to assign a quinonoid constitution to coloured compounds. He had himself found that the colourless lactone of 2 : 4 : 2′ : 4′-tetrahydroxydiphenylacetic acid dissolves in alkalis with a colour extremely like that produced by phenolphthalein, but the colour is discharged on breaking the lactone ring. He had not, however, been able to devise any plausible quinonoid formula for the salts of the lactone.

Prof. Green, replying to Mr. Baly, said that the assumption of an oxonium hydrate group in the alkali salts of phenolphthalein was not a necessary deduction from his experiments, but was only advanced in order to give a clearer expression to the analogy in behaviour between these salts and those of quinolphthalein, the latter of which must contain an oxonium group.

Mr. Baly's statement that a quinonoid compound containing oxonium hydrate groupings would be colourless did not rest on any experimental evidence known to him.

The conclusion that the esters described were quinonoid compounds was in no way deduced from their colour, but was a necessary consequence of the experimental facts adduced in the paper, and depended especially on the proof that the methyl group was attached to the carbonyl and the chlorine atom in the ester chlorides to oxygen. These facts, especially in the case of the trimethyl ether of quinolphthalein, scarcely admitted of any other interpretation than that given.

*193. "Ketene." By Norman Thomas Mortimer Wilsmore.

The gaseous substance produced by the action of a hot platinum wire on acetic anhydride, which was discovered by Dr. A. W. Stewart and the author (*Nature*, 1907, **75**, 510), has been further examined. As a mean result, it was found that, on exploding one volume of the gas with excess of oxygen, there was a contraction of 1·09 volumes, and that the residual gas contained 1·97 volumes of carbon dioxide, whilst 2·08 volumes of oxygen had disappeared. The corresponding numbers for a gas having the formula C_2H_2O would be 1 : 1 : 2 : 2. A mean value for the density gave a molecular weight of 41·4, instead of 42. The gas has, however, not yet been obtained entirely free from acetylene and higher hydrocarbons. Its marked tendency to condense

slowly, on standing, to a brown liquid is one of the chief difficulties in the way of its purification.

The substance combines directly with aniline to form acetanilide, with *o*-toluidine to form aceto-*o*-toluidide, with anhydrous liquid ammonia to form acetamide, and with ethyl and amyl alcohols to form the corresponding acetic esters. It also reacts vigorously with bromine, forming bromoacetyl bromide. As no by-products appear to be formed in these reactions, it may be inferred that the substance is a new anhydride of acetic acid, having the formula $CH_2{:}CO$ or $CH{:}C{\cdot}OH$, and, further, that it is the lowest member of the ketene series. With water, *ketene* gives chiefly acetic acid, but an aldehyde, probably glycollaldehyde, is formed at the same time. Ketene is also produced when an arc is made to burn under the surface of liquid acetic anhydride.

Discussion.

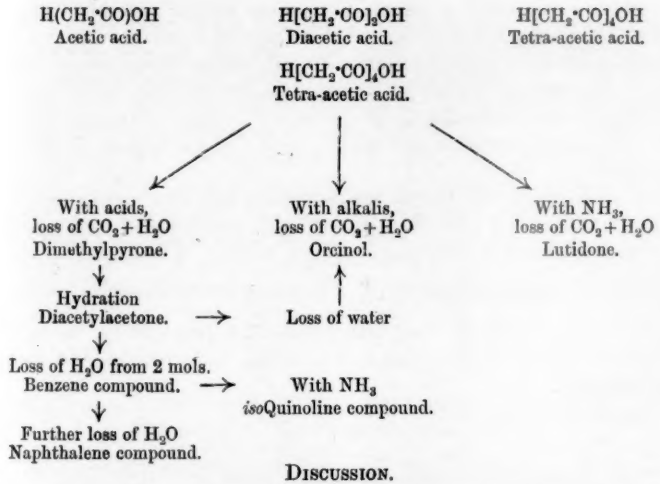
The President suggested that a third possible formula for ketene would be $\begin{matrix} HC \\ \| \\ HC \end{matrix}\!\!>\!O$, a substance having the same relation to acetylene as ethylene oxide has to ethylene. Such a compound might lend itself easily to polymerisation.

***194. "Derivatives of the multiple ketene group."**
By John Norman Collie.

The group $\cdot CH_2{\cdot}CO\cdot$ (which the author proposes to call the "*ketide*" group) can be made to yield by means of the simplest reactions a very large number of interesting compounds, all belonging to classes which are largely represented amongst the compounds obtained from plants.

Illustrations of this were given from the various published papers of the author. It was shown how by uniting more than one of these groups as in ethyl acetoacetate, $H[CH_2{\cdot}CO]_2OH$, or in dehydracetic acid, $H[CH_2{\cdot}CO]_4OH$, "*polyketides*" are obtained, and from these by means of the simplest reactions, such as hydration, dehydration, oxidation, reduction, loss of carbon dioxide, or action of ammonia, complicated polyketide derivatives result. These are found to represent many of the various types of compounds found in plants.

This can be partly illustrated as follows:



DISCUSSION.

Dr. M. O. FORSTER inquired what compounds, exactly, were to be classified as polyketides. The name naturally invited comparison with the words polymethylene and polypeptide, the significance of which was perfectly clear, and from that standpoint a polyketide would be a substance built up of the complex, $[\cdot CH_2 \cdot CO \cdot]_x$, with the necessary terminal groups or atoms. The application of the word in Prof. Collie's paper, however, was much more comprehensive, appearing to embrace such heterogeneous types as lactones, pyrone derivatives, benzenoid compounds, and substituted pyridines, and the speaker foresaw considerable danger in launching an entirely novel expression on chemical nomenclature without defining its scope more precisely.

***195. "Production of orcinol compounds by the action of heat on the sodium salt of ethyl acetoacetate." By John Norman Collie and Edwin Rodney Chrystall.**

When ethyl acetoacetate (78 grams) is mixed with sufficient sodium ethoxide (4·6 grams of sodium in 50 c.c. of ethyl alcohol) to convert about one-third of it into the sodium salt and the mixture heated, ethyl acetate, alcohol, and ethyl acetoacetate distil. On treating the viscous residue in the flask with hydrochloric acid, a crystalline compound separates, which is best purified by recrystallisation from benzene (yield about 7·8 grams). It has the composition $C_{16}H_{16}O_6$ and melts at 169°:

$$4C_6H_{10}O_3 = C_{16}H_{16}O_6 + CH_3 \cdot CO_2Et + 2EtOH + 2H_2O.$$

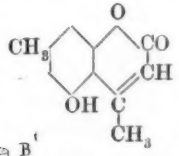
The new compound is soluble in aqueous sodium hydroxide with a deep yellow colour, but the colour changes to pale yellow on warming; acids precipitate from this solution an orange compound of high molecular weight, and alcohol is found in the residue. With sodium hydroxide and chloroform, it gives the orcinol reaction. With bromine, a compound of formula $C_{16}H_{15}O_6Br_3$, melting at 182·5°, is produced.

When warmed with 90 per cent. sulphuric acid to about 130—140°, carbon dioxide is evolved, together with alcohol and acetic acid, leaving a compound of formula $C_{11}H_{10}O_3$ melting at 250°:

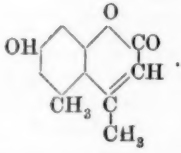
$$C_{16}H_{16}O_6 + 2H_2O = C_{11}H_{10}O_3 + CO_2 + EtOH + C_2H_4O_2.$$

This compound is identical with a substance prepared by von Pechmann and Cohen (*Ber.*, 1884, **17**, 2188) from orcinol and ethyl acetoacetate.

Its composition is either:



or



The *monomethyl ether* (m. p. 146°) and the *monoacetyl* derivative were prepared (m. p. 198°).

196. "A simple gas generator for analytical operations." By James McConnell Sanders.

The simple appliance described below has been found to be a convenient and practical substitute for the so-called "constant supply" apparatus of the "Kipp" type. It consists of a glass tube open at one end and having a fine, almost capillary, tube fused into the other end, as shown in the figure.

The apparatus is charged, for example, for the preparation of hydrogen sulphide by dropping one or two small fragments of ferrous sulphide into the tube so that they lodge in the annular space (*A*), a few drops of dilute sulphuric acid are then allowed to run into the tube, and the mouth (*B*) closed with the forefinger. The apparatus may then be introduced into a test-tube or beaker and used as an agitator, the gas escaping by way of the fine interior tube and the orifice (*C*).

For quantitative work, a larger apparatus is used and the mouth closed with a cork. For the preparation of a gas which requires the application of a gentle heat, the apparatus is allowed to touch the bottom of the test-tube while immersed in the liquid contents of the latter, and heat is applied to the test-tube itself.

After use, the generation of gas is instantly stopped by directing a stream of water from a wash-bottle into the interior, the outside is washed in the same manner, and the apparatus is then ready for use in a subsequent operation. The appliance has been in constant use in the Mexican Customs laboratories for the last five months, and in no case has it been found that the small inner tube showed any tendency to become clogged with precipitate.

197. "Some double ferrocyanides of calcium, potassium, and ammonium." By James Campbell Brown.

The conditions of preparation and the properties of calcium potassium ferrocyanide and calcium ammonium ferrocyanide were explained. These salts have been analysed and their solubilities determined. The calcium potassium ammonium ferrocyanides resulting from the mixture of varying proportions of calcium chloride, potassium ferrocyanide, and ammonium chloride were described, and the conditions for the use of ammonium chloride and potassium ferrocyanide as a qualitative test for calcium were given.

198. "Determination of halogen in organic substances." By James Moir.

The new method described last year by the author (*Proc.*, 1906, **22**, 261) has been improved by adopting the Volhard method of back-titration with standard thiocyanate.

The contents of the crucible after heating are dissolved and treated with a crystal of bisulphite to reduce manganate. A measured quantity of standard silver solution is added and the mixture is then acidified with nitric acid, heated to 70°, filtered through a Buchner funnel, using hardened paper, and the residue on the filter is extracted with hot dilute nitric acid. The filtrate is then cooled to 40° and titrated with standard thiocyanate and iron alum.

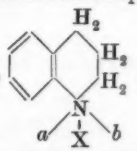
Each c.c. of *N*/10 silver solution, by difference, = 0·0080 gram of bromine.

199. "Racemisation by alkali as applied to the resolution of *r*-mandelic acid into its optically active isomerides." By Alex. McKenzie and Hermann August Müller.

It was shown that, as a product of the fractional saponification of *l*-menthyl *r*-mandelate in ethyl-alcoholic solution, either a dextrorotatory or a lævorotatory mandelic acid mixture may be obtained from the same weight of ester and using the same weight of alkali. The normal action is the formation of a dextrorotatory potassium salt; the formation of a lævorotatory potassium salt under the conditions quoted is abnormal.

Various methods of effecting the changes: (1) *r*-mandelic acid $\longrightarrow$ *r*-mandelic acid and *l*-mandelic acid and (2) *r*-mandelic acid $\longrightarrow$ *r*-mandelic acid and *d*-mandelic acid were indicated.

200. "The optical activity of cyclic ammonium compounds." By Frank Buckney and Humphrey Owen Jones.

Although it has been shown in a large number of cases that compounds of the type NabcdX can give rise to optical activity due to the asymmetric nitrogen atom, yet there is no well established case of activity when the nitrogen atom forms part of a ring. It was stated previously (*Trans.*, 1903, **83**, 1405) that substituted pyridinium compounds, quinolinium compounds, and tetrahydroquinolinium compounds of the type  are all devoid of a plane of symmetry and should be capable of giving rise to optical activity. Several compounds were then examined, but no evidence of activity was obtained.

The following fourteen compounds have now been examined: 1-methyl-α-picolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, methyl- and benzyl-quinolinium-*d*-camphorsulphonates-methylkairolinium-1-acetate-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-methyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate and *d*-bromocamphorsulphonate, 1-benzyl-1-ethyltetrahydroquinolinium-*d*-camphorsulphonate, benzylkairolinium-*d*-camphorsulphonate, *d*-bromocamphorsulphonate and tartrate, *n*-propylkairolinium-*d*-bromocamphorsulphonate, allylkairolinium-*d*-bromocamphorsulphonate. In the case of the last-mentioned compound only was there conclusive evidence of the existence of optical activity, the *l*-base *d*-acid salt

was the less soluble and had $[M]_D = 198°$, and the *d*-base *d*-acid had $[M]_D = 343°$. The iodide was recovered in small quantity only, but was decidedly active.

201. "The action of phosphorus pentachloride on hydroxytrimethylsuccinic ester. 1 : 2-Dimethyl*cyclo*propane-1 : 2-dicarboxylic acid (1 : 2-dimethyltrimethylene-1 : 2-dicarboxylic acid)." By Herbert Henstock and Bertha E. Woolley.

The authors have examined the chief chemical and physical properties of 1 : 2-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid (1 : 2-dimethyltrimethylene-1 : 2-dicarboxylic acid), the optical properties of its diethyl ester having been investigated for them by the late Sir William Perkin. The object of the work was to determine whether this constitution, which was assigned to the acid by Paolini (*Gazzetta*, 1900, **30**, ii, 497), is the correct one, since, if its saturated cyclic character were proved, an important difference is indicated in the behaviour of two so nearly allied substances as bromotrimethylsuccinic anhydride (which yields methylenedimethylsuccinic acid) and chlorotrimethylsuccinic ester when the hydrogen haloid is removed from the molecule. The authors' work confirms that of Paolini.

On the elimination of the hydrogen haloid from chlorotrimethylsuccinic ester, 1 : 2-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid is formed.

202. "The condensation of acetaldehyde and its relation to the biochemical synthesis of fatty acids." By Henry Stanley Raper.

It has been suggested that the formation of fatty acids, in animals, from carbohydrates depends, firstly, on a break-down of the carbohydrate to yield, amongst other products, acetaldehyde, and, secondly, on the condensation of the acetaldehyde leading to the formation of the higher fatty acids. The object of this investigation was to determine whether acetaldehyde on condensation yields the straight-chain compounds which would be necessary for the production of the higher fatty acids, as previous observations on the condensation of aldehydes point to the formation of compounds with branched-chains.

This objection to the above hypothesis has been partly removed, for it has been found that β-hydroxybutyraldehyde, the first product of the condensation of acetaldehyde, on further condensation yields an aldehyde containing eight carbon atoms united in a straight-chain.

203. "The influence of solvents on the rotation of optically active compounds. Part X. Effect of the configuration and degree of saturation of the solvent." By Thomas Stewart Patterson, Andrew Henderson, and Frank Walter Fairlie.

Solutions of ethyl tartrate in ethyl fumarate, ethyl maleate, and ethyl succinate were examined as regards rotation. Fumaric and maleic esters were found to have much the same effect, which is greater than the effect of succinic ester. The results were discussed from the point of view of combination of solute and solvent.

204. "Para-toluidine monohydrate." By James Walker and Heather Henderson Beveridge.

p-Toluidine crystallises from water and from aqueous alcohol as a monohydrate which melts at about 41·5°, the melting point of the anhydrous base being 43·5°. The monohydrate effloresces in the air, but, on the other hand, the anhydrous base absorbs water from air saturated with moisture, and is converted into the monohydrate. In contact with liquid water, the anhydrous base is converted into the monohydrate at all temperatures up to the melting point of the latter. The pressure of water vapour over the monohydrate at the ordinary temperature is somewhat more than half that of liquid water.

205. "Hydrates of some quaternary bases." By David Cowan Crichton.

Solutions of tetraethylammonium hydroxide, tetrapropylammonium hydroxide, and trimethylsulphine hydroxide were prepared from the corresponding chlorides by means of potassium hydroxide (compare Walker and Johnston, *Trans.*, 1905, **87**, 955).

A *tetrahydrate* and a *hexahydrate* of tetraethylammonium hydroxide were described. When the tetrahydrate is made to lose water at the ordinary temperature, the base decomposes with formation of triethylamine, ethylene, and water.

A *heptahydrate* of tetrapropylammonium hydroxide was separated by cooling the aqueous solution in a freezing mixture. This hydrate melts when raised to the ordinary temperature.

Attempts to prepare a crystalline hydrate of trimethylsulphine hydroxide were unsuccessful.

206. "Two volumetric methods for the determination of chromium." By Arnold William Gregory and James McCallum.

The authors have modified the persulphate method for the estimation of chromium in iron and steel, with the object of obtaining accurate results in a minimum time.

In the presence of manganese, the permanganic acid, formed simultaneously with the chromic acid, is reduced, either by the addition of a little ammonium chloride or by means of hydrogen peroxide.

The chromic acid formed is titrated with ferrous sulphate solution of known strength.

A method of oxidising the chromium with sodium bismuthate was also described. It is found to give very satisfactory results.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Beadle, *Clayton.* Chapters on papermaking. Vol. II. Comprising answers to questions on papermaking set by the examiners to the City and Guilds of London Institute. Vol. III. Comprising a short practical treatise in which boiling, bleaching, loading, colouring, and similar questions are discussed. Vol. IV. Containing discussions upon water supplies and the management of the paper machine and its influence upon the qualities of papers. pp. vii + 174, viii + 134, vii + 156. London 1906—1907. (*Recd.* 17/10/7.)
From the Author.

Curtius, *Theodor.* Festschrift Theodor Curtius zum 25 jährigen Doktor-Jubiläum gewidmet. Arbeiten aus dem Chemischen Institut der Universität Heidelberg von *G.* **Bredig,** *A.* **Darapsky,** *E.* **Ebler,** *H.* **Franzen,** *P.* **Jannasch,** *A.* **Klages,** *E.* **Knoevenagel,** *E.* **Mohr,** *R.* **Stollé.** pp. xc + 245. [pp. 1—245 reprinted from *Verhandl. d. Naturhist.-Med. Vereins.* N.F. 1907, 9.] Heidelberg 1907. (*Recd.* 31/7/7.) From Geheimrat Professor Dr. Theodor Curtius.

Dibdin, *W. J.* Recent improvements in methods for the biological purification of sewage. 2nd edition. pp. 68. ill. London 1907. (*Recd.* 18/7/7.) From the Author.

Fischer, *Emil.* Untersuchungen in der Puringruppe (1882—1906). pp. viii + 608. Berlin 1907. (*Recd.* 30/9/7.) From the Author.

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 9th, 1907.

Those Fellows who received grants in December, 1906, or whose grants allotted in December of previous years have not been closed, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, Decembe 2nd, next.

At the next Ordinary Meeting on **Thursday**, November **7th**, 1907, at **8.30** p.m., the following papers will be communicated:

"Gaseous nitrogen trioxide." By H. B. Baker and Mrs. M. Baker.

"The atomic weight of tellurium." By H. B. Baker and A. H. Bennett.

"The isomerism of the double sulphites of sodium and potassium." By M. H. Godby.

"Studies in the camphane series. Part XXIV. Camphoryldithiocarbamic acid and camphorylthiocarbimide." By M. O. Forster and T. Jackson.

"The vapour pressures of triethylamine, of 2:4:6-trimethylpyridine, and their mixtures with water." By R. T. Lattey.

"Liquid triethylamine." By R. T. Lattey.

"The action of hydrogen sulphide on solutions of sodium hyposulphite." By F. S. Sinnatt.

"The alkyl compounds of gold. Diethylauric bromide. Preliminary note." By W. J. Pope and C. S. Gibson.

"Note on the constitution of homoeriodictyol." By F. B. Power and F. Tutin.

"The interaction of methylene chloride and the sodium derivative of ethyl malonate." By F. Tutin.

"Preparation of aliphatic nitro-compounds by the interaction of the alkyl iodides and mercurous nitrite." By P. C. Rây and P. Neogi.

"Some mercury derivatives of camphor." By J. E. Marsh and R. de J. F. Struthers.

"Contribution to the chemistry of the terpenes. II. The oxidation of limonene with chromyl chloride." By G. G. Henderson.

"The synthesis of acridines and phenonaphthacridines: Tetra- and hexa-methylacridines: Dimethylphenonaphthacridines: Dixylylmethylenediamines." By A. Senier and A. Compton.

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Issued 16/11/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 331.

Thursday, November 7th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

Messrs. P. C. Austin, C. Hollins, and L. G. Killby were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Edward de Barry Barnett, 40, Queensborough Terrace, Hyde Park, W.
Frederic William Caton, B.A., B.Sc., 6, King Street, Snow Hill, E.C.
George Hugh Crisp, B.A., 62, Gainsboro' Road, Crewe.
Claude Scott Fawcitt, Darlington, England; and Shimoga S.M.Ry., India.

Of the following papers, those marked * were read:—

***207. "Gaseous nitrogen trioxide." By Herbert Brereton Baker and Muriel Baker.**

The authors have found that liquid nitrogen trioxide can be converted into the gaseous state if it is dried completely. Seventeen determinations of the density of the gas have been made by Victor Meyer's method in very dry nitrogen. Several different prepara-

tions were used and the densities varied from 38 to 62. The density corresponding to the formula N_2O_3 is 38, and it is concluded that there is partial polymerisation to the double molecule N_4O_6. The analysis of the substance gave 63·12 per cent. of oxygen (mean of 5 experiments), the calculated value for the trioxide being 63·09. Determinations of the molecular weight by the cryoscopic method in dried benzene gave 83 and 83·2 for one sample and 95 for another. The liquid is green at the ordinary temperature, but becomes blue below $-2°$. It does not solidify at $-80°$, but in liquid air it solidifies to a mass of very dark blue crystals.

Discussion.

Dr. Veley asked if the authors had examined the effect of sunlight on nitrogen trioxide, as it appeared possible that the variations in composition and density of the several samples examined might be due to this cause.

The observation of the authors that nitrogen trioxide does not dissolve in water to form nitrous acid, as such, seemed of especial interest; although this acid was frequently represented as a reagent in chemical change, yet those who had worked on the subject had begun to realise that nitrous acid was possibly no better than a convenient fiction.

Dr. Divers called attention to the fact that, two years ago, Raschig (*Zeitsch. angew. Chem.*, 1905, **18**, 1281), and Rây and Gañguli (*Proc.*, 1905, **21**, 280), showed, independently, that nitric oxide distinctly forms nitrogen trioxide with oxygen before it goes on to produce nitric peroxide, and thus furnished chemical evidence, for the first time, of the existence of nitrous anhydride, N_2O_3, in the gaseous state.

Dr. Baker, in reply, stated that sunlight had not been observed to exert any effect on nitrogen trioxide.

***208. "The atomic weight of tellurium." By Herbert Brereton Baker and Alexander Hutcheon Bennett.**

The investigation of tellurium and the possibility of its containing another element has been the subject of study for the last thirteen years. The following methods were used in attempting to split up the element. (1) Fractional crystallisation of telluric acid prepared by two distinct processes. (2) Solution of barium tellurate in water. (3) Fractional distillation of (*a*) tellurium, (*b*) tellurium tetrachloride,

and (*c*) tellurium dioxide. (4) Conversion of tellurium into the hydride. (5) Fractional electrolysis of tellurium tetrachloride and tetrabromide. (6) Fractional precipitation of tellurium tetrachloride by water.

In none of these processes was any difference found in the various fractions. Two methods were described for finding the equivalent of the element. The first, which depends on the reduction of the dioxide to the element by means of sulphur, gave 127·60 as the atomic weight (mean of 25 determinations), and the second, depending on the conversion of the element into the tetrabromide, gave 127·61 (mean of 18 determinations).

Discussion.

The President remarked that no research is final, but this one must go a long way to settle the question of the homogeneity of tellurium.

Dr. Percy Williams, many years ago, carried out at University College some experiments on the subject. Tellurium, purified by crystallisation of its double bromide with potassium, gave, on reducing its oxide with hydrogen and absorbing volatilised metal with silver foil, the number 127·6 for the atomic weight. The double bromide, owing to the crystals retaining mother-liquor, was not adapted for an atomic weight determination.

*209. "The isomerism of the double sulphites of sodium and potassium." By Michael Harry Godby.

By neutralising potassium hydrogen sulphite with sodium hydroxide and sodium hydrogen sulphite with potassium hydroxide, two solutions are produced from which opaque, greasy crystals are obtained with some difficulty. They are of somewhat variable composition as regards water of crystallisation, and contain the metals in unequal atomic proportions, generally about 60 atoms of sodium to 40 of potassium.

These crystals, when heated with ethyl iodide to 130—140° in a sealed tube, yield a salt which can be crystallised from boiling alcohol and contains ethyl, sodium, potassium, iodine, and SO_3. In each case, there are present about 76 atoms of potassium for every 24 of sodium.

An attempt was made to prepare the double sulphites from the two solutions by precipitating with alcohol, as recommended by Rohrig. Fine powdery, white crystals were obtained having almost exactly the composition required for $KNaSO_3$.

These crystals, when heated with ethyl iodide as before and the product extracted with boiling alcohol, gave a white, finely-crystalline salt, which was recrystallised from boiling alcohol. This salt, whether obtained from the solution made originally by neutralising potassium hydrogen sulphite with sodium hydroxide or by neutralising sodium hydrogen sulphite with potassium hydroxide, contained sodium, potassium, ethyl, SO_3, and iodine in the same proportions, and approximated fairly closely to the salt prepared by Schwicker (*Ber.*, 1889, **22**, 1728) to which he ascribes the formula $4(KEtSO_3)NaI$, but contained 28 atoms of sodium to 72 of potassium, instead of 20 to 80 respectively.

There is no evidence for the existence of two isomeric salts, $KO{\cdot}SO_2Na$ and $NaO{\cdot}SO_2K$.

***210. "Studies in the camphane series. Part XXIV. Camphoryldithiocarbamic acid and camphorylthiocarbimide." By Martin Onslow Forster and Thomas Jackson.**

Camphoryldithiocarbamic acid, $C_8H_{14}<\begin{matrix}CH{\cdot}NH{\cdot}CS{\cdot}SH\\ |\\ CO\end{matrix}$, prepared from aminocamphor and carbon disulphide, is much more stable than compounds of this class which have been hitherto described, and does not decompose below its melting point, 128°. The *methyl* ester, $C_{12}H_{19}ONS_2$, melts at 147°, and is resolved into camphorylthiocarbimide and methyl mercaptan at 170°; the *benzoyl* derivative, $C_{18}H_{21}O_2NS_2$, crystallises from petroleum in colourless, silky needles melting at 105°. Nitrous acid oxidises the dithiocarbamic acid to the thiocarbimide and sulphur, but if amyl nitrite is added to an ethereal solution of the acid an intermediate *compound*, $C_{11}H_{15}ONS_2$, is produced, which melts at 110°, and breaks up readily into sulphur and the mustard oil.

Camphorylthiocarbimide, $C_8H_{14}<\begin{matrix}CH{\cdot}N{:}C{:}S\\ |\\ CO\end{matrix}$, obtainable in a variety of ways from the dithiocarbamic acid, melts at 106·5°, and combines readily with bases, but less freely with alcohols; *camphorylthiocarbamide*, $C_{11}H_{18}ON_2S$, arising from it by the action of dry ammonia, melts at 180°, and *dicamphorylthiocarbamide*, $C_{21}H_{32}O_2N_2S$, obtained by prolonged treatment with water, melts at 176°. *Camphorylphenylthiosemicarbazide*, $C_{17}H_{23}ON_3S$, occurs in two modifications, melting at 183° and 163° respectively; these are distinguishable by a variety of colour reactions, and by the readiness with which the less fusible form passes into the *anhydride*, $C_{17}H_{21}N_3S$, which melts at 235°.

Discussion.

Mr. W. C. Reynolds observed that supersaturated solutions of the alkaloid hyoscyamine in some solvents, such as water and wet ether, behaved in a similar manner to the case described by Dr. Forster.

Mr. A. C. Chapman remarked that the glucoside apiin was another substance in which a remarkable relationship existed between the jelly and the crystalline forms.

The President suggested the analogy between the phenomena mentioned by Dr. Forster and other gentlemen and superfusion. Alcohol, when cooled, solidifies to a glass; on standing for a couple of days, crystallisation sets in, as indeed it does in the long run with ordinary glass. In the instances adduced by Dr. Forster, no doubt surface tension phenomena are concerned.

***211. "The vapour pressures of triethylamine, of 2 : 4 : 6-trimethylpyridine, and of their mixtures with water." By Robert Tabor Lattey.**

A study of the total pressure curves for these mixtures shows that they conform to the type predicted by theory. The partial pressure curves can be calculated by a form of the Duhem-Margules equation. In both cases the curves show a maximum where the compositions of vapour and liquid are identical. At temperatures where the miscibilities of the components are limited there are indications of a second maximum inside the "unreal" parts of the curves.

***212. "Liquid triethylamine." By Robert Tabor Lattey.**

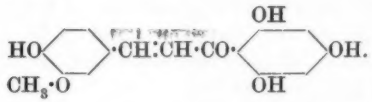
A comparison of the vapour pressures and critical constants of triethylamine and other liquids leads to the belief that the amine is a unimolecular liquid. This is confirmed by a determination of the temperature-coefficient of the molecular surface energy.

***213. "Note on the constitution of homoeriodictyol." By Frederick Belding Power and Frank Tutin.**

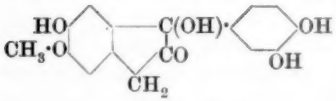
At the meeting of the American Pharmaceutical Association held in September, 1906, a paper was communicated by the authors entitled "Chemical Examination of Eriodictyon" (*Proc. Amer. Pharm. Assoc.*, 1906, **54**, 352; Abstr., 1906, ii, 885). In this communication, we described the isolation and properties of three new crystalline sub-

stances, one of which possessed the formula $C_{16}H_{14}O_6$, and was designated homoeriodictyol. Early in the following year, G. Mossler (*Annalen*, 1907, **351**, 233) described the results of an examination of the same drug. Mossler had also isolated from *Eriodictyon* leaves the substance possessing the formula $C_{16}H_{14}O_6$, but proposed to name it "eriodictyonon."

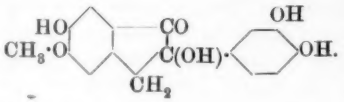
At the time of the appearance of the latter paper, we were engaged in further work on homoeriodictyol, the results of which (*Trans.*, 1907, **91**, 889) led us to assign to this substance the following constitutional formula:



We have recently been favoured by Dr. Mossler with a reprint of a paper communicated by him to the Academy of Sciences in Vienna (*Sitzungsber. K. Akad. Wiss. Wien.*, 1907, **116**, ii, June, 1907) at a time when he was unaware of our second investigation. In this most recent paper, he sets forth the conclusion that homoeriodictyol ("eriodictyonon") is represented by one of the following formulæ:



or



It is stated by Mossler that the action of alkalis on homoeriodictyol results only in the formation of a red resin, but this is not the case, as it was shown in our second communication that the product of this action, although highly coloured and containing a considerable amount of tarry matter, consists to a large extent of a mixture of phloroglucinol and ferulic acid. It follows from this that neither of the above formulæ proposed by Mossler can correctly represent the constitution of homoeriodictyol, as substances possessing such configurations could not possibly give rise to phloroglucinol. On the other hand, a ready explanation of the formation of all the substances obtained from homoeriodictyol by Mossler is afforded by assigning to this compound the constitution which we have proposed.

Although the observation, recorded by Mossler, that the action of bromine on homoeriodictyol is one of substitution, and not of addition, might be taken as evidence in support of the conclusion that the latter

substance was saturated, it cannot be considered as proof that an ethylenic linking is not present.

The statement made by Mossler that homoeriodictyol possesses optical activity, is in direct conflict with our views regarding the constitution of this substance, as the formula we have proposed contains no asymmetric carbon atom. We had previously examined tetra-acetylhomoeriodictyol polarimetrically, but without being able to detect any optical activity, and have now repeated this experiment with the same result. Homoeriodictyol, also, has now been examined in this direction, and we can definitely state that our material is optically inactive. So far as we are aware, therefore, no facts have yet been recorded which are not in harmony with the formula we have assigned to homoeriodictyol.

214. "The alkyl compounds of gold. Diethylauric bromide." (Preliminary note.) By William Jackson Pope and Charles Stanley Gibson.

Auric bromide reacts vigorously with magnesium ethyl bromide in ethereal solution, and from the product *diethylauric bromide*, $(C_2H_5)_2AuBr$, has been separated; this is the first alkyl gold compound to be described.

Diethylauric bromide dissolves in the ordinary organic solvents, but is insoluble in water. It crystallises in long, colourless needles which melt at 58° with slight decomposition; on rapid heating, it decomposes explosively at about 70°. The compound has an odour resembling that of bromocamphor, and volatilises on warming in a vacuum. It is much more readily acted on by reagents than is the recently discovered trimethylplatinic iodide, $(CH_3)_3PtI$; thus the former yields crystalline products on treatment with ammonia and nitric acid, whilst the latter is unaffected by those reagents.

The study of the alkyl compounds of the metals of groups I and VIII of the periodic classification is being continued.

215. "The interaction of methylene chloride and the sodium derivative of ethyl malonate." (A correction.) By Frank Tutin.

In a paper bearing the above title (*Trans.*, 1907, **91**, 1141), three crystalline substances were described as by-products of the reaction which takes place when methylene chloride is heated with the sodium derivative of ethyl malonate. It has now been ascertained that one of

these substances, described as "the yellow sodium salt," is the sodium derivative of "ethyl dicarboxyglutaconate," and had been formed from chloroform which was present as an impurity in the methylene chloride. The acid obtained by the hydrolysis of this sodium compound, and to which the formula $C_{10}H_{12}O_8$ was assigned, must, therefore, have been glutaconic acid, $C_5H_6O_4$.

216. "Preparation of aliphatic nitro-compounds by the interaction of the alkyl iodides and mercurous nitrite." By Prafulla Chandra Rây and Pañchañan Neogi.

By the interaction of mercurous nitrite and the alkyl iodides, namely, methyl, ethyl, *iso*propyl, and *iso*amyl iodides, the corresponding nitro-compounds and the esters are formed. In this respect, mercurous nitrite behaves exactly like silver nitrite. The yields obtained were as follows: [(*a*) = with silver nitrite, (*b*) = with mercurous nitrite]. Methyl iodide (28 grams) gave (*a*) methyl nitrite, 3·6 grams, and nitromethane, 4·0 grams, (*b*) 2·1 grams and 2·6 grams respectively. Ethyl iodide (60 grams) gave (*a*) ethyl nitrite, 12·8 grams, and nitroethane, 12·1 grams, (*b*) 8·8 grams and 9·2 grams respectively. *iso*Propyl iodide (34 grams) gave (*a*) *iso*propyl nitrite, 8·0 grams, and nitro*iso*propane, 6·3 grams, (*b*) 4·1 grams and 3·8 grams respectively.

*iso*Amyl iodide (76 grams) gave (*a*) *iso*amyl nitrite, 3·2 grams, and nitro*iso*pentane, 12·4 grams, (*b*) 3·2 grams and 7·8 grams respectively.

217. "Some mercury derivatives of camphor." By James Ernest Marsh and Robert de Jersey Fleming Struthers.

When camphor is heated with an alkaline solution of mercuric iodide, mercury derivatives of camphor are formed. By treatment with glacial acetic acid, *camphor dimercuri-iodide*, $C_{10}H_{14}O,Hg_2I_2$, is precipitated. The filtrate, when diluted with water, gives with potassium iodide, or, better, with a solution of mercuric iodide in potassium iodide, an orange precipitate of the double salt, $C_{10}H_{15}O,HgI + HgI_2$ This, on treatment with potassium iodide in neutral solution, gives *camphor mercuri-iodide*, $C_{10}H_{15}O,HgI$, which is pale yellow. The above-mentioned acetic acid solution also gives with potassium chloride and bromide white precipitates of *camphor mercurichloride*, $C_{10}H_{15}O,HgCl$, and *camphor mercuribromide*, $C_{10}H_{15}O,HgBr$, respectively, which, however, have not yet been obtained quite free from iodide.

218. "Contributions to the chemistry of the terpenes. Part II. The oxidati of limonene with chromyl chloride." By George Gerald Henderson.

When a dilute solution of chromyl chloride in carbon disulphide is slowly added to a similar solution of limonene, an *additive product*, $C_{10}H_{16},2CrO_2Cl_2$, is precipitated. This compound is a brown powder, which begins to decompose in moist air, and at once reacts with water, yielding a solution of chromic chloride, some resinous matter, and a brown, viscous liquid insoluble in water. When subjected to distillation in steam, the brown liquid yields a further quantity of resinous matter and a clear yellow oil, which is composed of an aldehyde, a ketone, and a very unstable substance containing chlorine as well as oxygen. The *aldehyde*, $C_{10}H_{14}O$, is a strongly odorous, oily liquid, b. p. 221—222°/755 mm. It yields a crystalline *semicarbazone*, m. p. 156°. It is unsaturated, and on exposure to air it is converted into the corresponding *acid*, $C_{10}H_{14}O_2$, which forms small, colourless crystals, m. p. 172°. The *silver* salt of the acid crystallises in small, white prisms. Boiling dilute nitric acid converts the aldehyde slowly into *p*-toluic acid; this is also the chief product when the aldehyde is oxidised with a dilute solution of potassium permanganate. The *ketone*, $C_9H_{12}O$, is the chief constituent of the oxidation product. It is an almost colourless, oily liquid with a strong odour, b. p. 112—113°/15 mm. It is unsaturated. The *semicarbazone* of the ketone crystallises with one molecule of methyl alcohol in colourless prisms which quickly effloresce in the air. After heating at 100°, it melts at 205°. When heated with ammonium formate in a sealed tube, the ketone is converted into the formyl derivative of an amine, from which the free *amine*, $C_9H_{13}\cdot NH_2$, is obtained by hydrolysis with alcoholic potash. It is a colourless, oily liquid with a disagreeable odour and an alkaline reaction, and is almost insoluble in water. The hydrochloride and the sulphate of the amine are deliquescent and very readily soluble in water or alcohol; the *platinichloride*, which is very sparingly soluble in water, crystallises in small, brownish-yellow needles. The chlorinated oxidation product is so unstable that it could not be isolated.

219. "The synthesis of acridines and phenonaphthacridines: tetra- and hexa-methylacridines: dimethylphenonaphthacridines: di-xylylmethylenediamines." By Alfred Senier and Arthur Compton.

By the interaction of methylene dichloride and xylidines, with or without xylenols, two methylenediamines are formed which by means

of Ullmann's method of substitution (*Ber.*, 1903, **36**, 1019) give rise to two corresponding acridines. One of the latter can also be obtained by heating the methylenediamine to a higher temperature, whereas the other cannot. This is explained by assuming that, when the *p*-position with respect to the amino-group in the arylamine is not substituted, the methylenediamine first formed is changed by metastasis to a methylenebenzidine (*pp*-diaminodiarylmethane) from which no acridine can result.

When, however, the *p*-position is occupied by an alkyl group, the metastatic action produces an *oo*-diaminodiarylmethane from which an acridine is easily derived. By the interaction of methylene dichloride and mixtures of xylidines and naphthols, corresponding dimethylphenonaphthacridines are obtained.

The following compounds were described. *Di*-1 : 3 : 4-*xylylmethylenediamine* (compare Senier and Goodwin, *Trans.*, 1902, **81**, 284). 1 : 3 : 7 : 9-*Tetramethylacridine*; its *platinichloride*, *aurichloride*, and *picrate*. *Di*-1 : 4 : 5-*xylylmethylenediamine* and its *platinichloride*. 1 : 4 : 6 : 9-*Tetramethylacridine* and its *aurichloride*. 1 : 3 : 4 : 6 : 7 : 9-*Hexamethylacridine* (compare Senier and Goodwin, *loc. cit.*). *Di*-ψ-*cumylmethylenediamine*. 9 : 11-*Dimethylpheno*-$\overset{\text{N-}\alpha}{\underset{\text{CH}\beta}{|}}$-*naphthacridine* and its *platinichloride*. 9 : 11-*Dimethylpheno*-$\overset{\text{N-}\beta}{\underset{\text{CH}\alpha}{|}}$-*naphthacridine* (compare Ullmann, *Chem. Centr.*, 1901, ii, 568). 8 : 11-*Dimethylpheno*-$\overset{\text{N-}\alpha}{\underset{\text{CH}\beta}{|}}$-*naphthacridine* and its *platinichloride*. 8 : 11-*Dimethylpheno*-$\overset{\text{N-}\beta}{\underset{\text{CH}\alpha}{|}}$-*naphthacridine* and its *platinichloride*.

220. "Chemical examination of the root and leaves of Morinda longiflora." By Marmaduke Barrowcliff and Frank Tutin.

The root and leaves of *Morinda longiflora*, G. Don, a West African plant known as "Ojuologbo," and stated to possess valuable medicinal properties (*Journ. Soc. Arts.*, 1905, **53**, 1069), have been chemically examined.

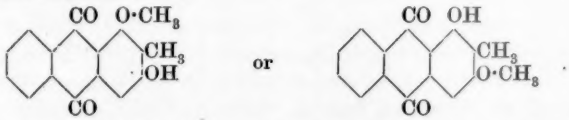
The ground materials were extracted with hot alcohol, and the resulting extracts separately investigated. No alkaloid was present in either material.

The extract yielded by the root gave a small quantity of a *hydroxymethoxymethylanthraquinone*, $C_{16}H_{12}O_4$ (m. p. 290°), and a small amount of a monoethyl ether of alizarin. It also yielded, in addition to resins and other amorphous products, formic, acetic,

butyric, palmitic, and citric acids, a phytosterol, $C_{27}H_{46}O$ (m. p. 130°), and a large amount of a sugar which gave *d*-phenylglucosazone (m. p. 215°).

The extract of "Ojuologbo" leaves gave, in addition to some of the substances mentioned above, a small amount of the hydrocarbon hentriacontane, and a new, crystalline *alcohol*, $C_{38}H_{61}O_3{\cdot}OH$ (m. p. 278°; $[\alpha]_D + 65{\cdot}9°$), designated *morindanol*. This compound, on treatment with sodium ethoxide and methyl iodide, yields *methylmorindanol*, $C_{38}H_{61}O_3{\cdot}OCH_3$ (m. p. 116°).

The above-mentioned hydroxymethoxymethylanthraquinone yields, on methylation, 1 : 3-*dimethoxy*-2-*methylanthraquinone* (m. p. 181°), and, on heating with 70 per cent. sulphuric acid, it gives 1 : 3-dihydroxy-2-methylanthraquinone. It must therefore be represented by one of the following formulæ:



On heating with hydriodic acid, it yields a *dihydroxymethylanthranol*, $C_{15}H_{12}O_3$ (m. p. 235°).

The monomethyl ether of alizarin is identical with the compound of this nature which was isolated by Perkin and Hummel (*Trans.*, 1893, **63**, 1174) from "Chay root."

Neither of the extracts possessed any pronounced physiological activity.

221. "Ethyl α-cyano-γ-phenylacetoacetate."

By Arthur Richard Smith and Jocelyn Field Thorpe.

Contrary to the observation of Haller, it is found that ethyl α-cyano-γ-phenylacetoacetate, $CH_2Ph{\cdot}CO{\cdot}CH(CN)CO_2Et$, is a well-defined, crystalline substance, which melts at 25°, and distils without decomposition at 178° (20 mm.). The compound is a strong acid, readily decomposing carbonates, and yielding salts which can be recrystallised from water without undergoing dissociation. The alkali salts are not acted on by alkyl iodides, but if the silver salt is treated, in dry ether solution with ethyl iodide a mixture of *ethyl α-cyano-γ-phenyl-α-ethylacetoacetate*, $CH_2Ph{\cdot}CO{\cdot}CEt(CN)CO_2Et$, and *ethyl α-cyano-β-ethoxy-γ-phenylcrotonate*, $CH_2Ph{\cdot}C(OEt){:}C(CN)CO_2Et$, is produced. The former is a liquid boiling at 190—191° (20 mm.), and the latter a solid melting at 66°. Characteristic derivatives of ethyl α-cyano-γ-phenylacetoacetate and of the two forms of its ethyl derivative were described.

222. "Aromatic amides and imides of camphoric acid." By William Ord Wootton.

The substance obtained by the action of nitrous acid on camphorylphenylhydrazide is found to be N-*nitrosocamphorylphenylhydrazide*, $C_8H_{14}\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot N(NO)\cdot C_6H_5$, m. p. 157°, and not a nitro-compound as stated by E. M. Chaplin (*Ber.*, 1892, **25**, 2565). N-*Nitrocamphorylphenylhydrazide*, $C_8H_{14}\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot N(NO_2)\cdot C_6H_5$, may be prepared by the action of nitric acid and acetic anhydride on camphorylphenylhydrazide, and forms colourless prisms melting and decomposing at 115—116°.

Camphoryl-4-bromophenylhydrazide, $C_8H_{14}\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot NH\cdot C_6H_4Br$, and *camphoryldibromophenylhydrazide* have been prepared, together with their N-*nitroso*- and N-*nitro*-derivatives. It is found in each case that the nitroso-derivatives are pale yellow, whilst the nitro-compounds are colourless. The fact that the latter are readily reduced with elimination of ammonia indicates that the nitro-group is not attached to the benzene nucleus.

Camphoric anhydride combines with *p*-bromoaniline at 120° to form *4-bromophenyl-α-camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4Br$, m. p. 207°. Reduction of the *nitro*-derivative of this acid yields *4-bromo-3-aminophenyl-α-camphoramic acid*, m. p. 207°. *4-Bromo-3-aminophenylcamphorimide*, $C_8H_{14}\langle\begin{matrix}CO\\CO\end{matrix}\rangle N\cdot C_6H_3Br\cdot NH_2$, has also been obtained. These two amino-compounds are optically active, and it is the author's intention to utilise them and certain of their derivatives in the study of racemic aldehydes.

Camphoric anhydride and aminoazobenzene combine to form *4-benzeneazophenyl-α-camphoramic acid*,

$$CO_2H\cdot C_8H_{14}\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_6H_5,$$

m. p. 223—224°. On reduction, *4-aminophenyl-α-camphoramic acid* is obtained.

223. "The melting point of *d*-phenylglucosazone." By Frank Tutin.

During the past few years a number of plants have been submitted to exhaustive investigation in the Wellcome Chemical Research Laboratories, and in all cases where sugar was found to be present the osazones were prepared. In a number of instances the phenylosazone obtained melted at a temperature considerably higher than that at which *d*-phenylglucosazone is stated to fuse, namely 205°. Several of

these preparations melted at or above 215°, whilst the osazone yielded by the sugar contained in the leaves of *Gymnema sylvestre* (Power and Tutin, *Pharm. J.*, 1904, **73**, 234) fused at 218—219°. Analyses of these preparations of high melting point showed that they were the osazones of hexoses, and as the only compound of this class stated to melt above 206° is α-acrosazone (m. p. 217°), it was at first thought that they must be identical with this compound and were derived from inactive sugars.

It was, therefore, deemed of importance to recrystallise and examine a number of the specimens of osazones which had been prepared from plant sugars by different workers in these laboratories. With this end in view experiments were instituted with the object of finding a better means of purifying osazones than by recrystallisation from alcohol, and it was ascertained that the use of pyridine was attended with excellent results. The osazone was dissolved in a small quantity of boiling pyridine, hot alcohol and subsequently a little water added, when, on allowing the mixture to cool, the osazone separated in a pure condition.

Specimens of osazones prepared from plant sugars were then recrystallised in this manner, with the results shown in the following table:

Source of sugar.	Original melting point of osazone.	Melting point after recrystallisation.
Brucea antidysenterica (fruit)	205°	217°
,, ,, (bark)	205	215—216
Gymnema sylvestre (leaves)	218—219	217
Aethusa cynapium (herb)	218	217
Grindelia camporum (herb)	205—206	216
Chailletia toxicaria (fruit).....	211—212	216
Eriodictyon Californicum (leaves)...	205	216—217
Morinda longiflora (root)	215	216
Lippia scaberrima (herb)	210	216—217
Ipomoea purga (tuber)	217—218	217—218
Olea Europaea (bark).....	216	217
Micromeria Chamissonis (herb)... ..	205	217

A specimen of *d*-phenylglucosazone (from dextrose) melting at 205° was then recrystallised in a similar manner, after which it melted at 217°. Furthermore, it was found that *d*-phenylglucosazone, when prepared from dextrose by the aid of freshly distilled phenylhydrazine, and avoiding a too protracted period of heating, exhibited an initial melting point of 216°.

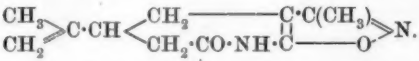
It is evident, therefore, that *d*-phenylglucosazone, when pure, melts at about 217°, and not at 205° as stated by Fischer (*Ber.*, 1884, **17**, 579).

On referring to the original papers on the subject it will be found that α-acrosazone was originally obtained melting at 205° (Fischer and Tafel, *Ber.*, 1887, **20**, 1093), and that it was only after careful purification that it exhibited a melting point of 217° (*ibid.*, p. 3389). It is

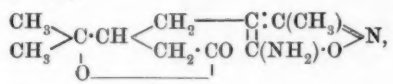
evidently owing to the fact that *d*-phenylglucosazone was not submitted to an equally elaborate process of purification (*loc. cit.*) that the correct melting point of this substance was not initially observed.

224. "The interaction of cyanodihydrocarvone, amyl nitrite and sodium ethoxide. Part II. The constitution of the products." By Arthur Lapworth and Elkan Wechsler.

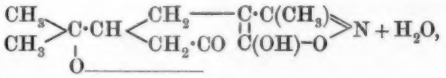
The compound obtained as the product in the above reaction and referred to in the first paper (*Trans.*, 1907, **91**, 978) as "the lactam" (*L*), has the constitution :



The derived amino-acid (*A*), when acted on by acids, is converted into the "lactonic base" (*B*),

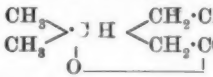


and the "lactonic acid,"



successively.

On reduction with ferrous hydroxide in alkaline solution, the latter yields pure *d*-homoterpenoyl methyl ketone,



ammonia and carbonate.

The isomeric "lactonic base" (*B'*), erroneously assigned $[\alpha]_D$ 6·21, is quite inactive and on reduction yields inactive homoterpenoyl methyl ketone. This base is therefore a racemic form of *B*. The isomeric lactam (*L'*), is strongly active, but also yields the inactive keto-lactone on reduction.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Hazen, *Allen.* Clean water and how to get it. pp. x + 178. ill. New York [1907]. (*Recd.* 16/10/7.)

From the Publishers: Messrs. John Wiley and Sons.

Luxmoore, *C. M.* The soils of Dorset. A report on their mechanical and chemical composition and on their physical properties. pp. 36. 1907. (*Recd.* 14/10/7.) From the Author.

Martin, *Geoffrey.* Practical chemistry for army and matriculation candidates. pp. viii + 144. ill. London 1907. (*Recd.* 5/10/7.)

From the Publishers: Messrs. Crosby Lockwood and Son.

Muir, *M. M. Pattison.* A history of chemical theories and laws. pp. xx + 555. New York 1907. (*Recd.* 17/7/7.)

From the Publishers: Messrs. John Wiley and Sons.

Nissenson, *H.* Die Untersuchungsmethoden des Zinks unter besonderer Berücksichtigung der technisch wichtigen Zinkerze. (Die chemische Analyse, Vol. II.) pp. 140. Stuttgart 1907. (*Rec* 31/7/7.) From the Publisher: Ferdinand Enke.

Palmer, *John Dabney.* Practical test-book of chemistry. pp. x + 190. New York 1907. (*Recd.* 16/9/7.)

From the Publishers: Messrs. John Wiley and Sons.

Royal Society of London. Some account of the "classified papers" in the archives. With an index of authors. Compiled by *A. H.* **Church.** pp. 38. Oxford 1907. (*Recd.* 11/10/7.)

From Professor A. H. Church, F.R.S.

Schmidt, *Julius.* Die Anwendung der Hydrazine in der analytischen Chemie. (Die chemische Analyse, Vol. I.) pp. 92. Stuttgart 1907. (*Recd.* 31/7/7.) From the Publisher: Ferdinand Enke.

Seidell, *Atherton.* Solubilities of inorganic and organic substances. A handbook of the most reliable quantitative solubility determinations. pp. x + 367. New York and London. (*Recd.* 31/7/7.)

From the Publishers: Messrs. Crosby Lockwood and Son.

II. *By Purchase.*

Archiv für experimentelle Pathologie und Pharmakologie. Edited by *B.* **Naunyn** and *C.* **Schmiedeberg.** Vol. LVI, &c. Leipzig 1907 +.

Arrhenius, *Svante.* Theories of chemistry. Being lectures delivered at the University of California, in Berkeley. Edited by *T. Slater* **Price.** pp. xii + 212. London 1907. (*Recd.* 26/6/7.)

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 9th, 1907.

All persons who received grants in December, 1906, or in December of any previous year whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, December 2nd, next.

At the next Ordinary Meeting on **Thursday**, November **21st**, 1907, at **8.30** p.m., the following papers will be communicated :

"The interaction of metallic sulphates and caustic alkalis." By S. P. U. Pickering.

"The chemistry of Bordeaux mixture." By S. P. U. Pickering.

"Aromatic azoimides. Part III. The naphthylazoimides and their nitro-derivatives." By M. O. Forster and H. E. Fierz.

"Studies of dynamic isomerism. Part VII. Note on the action of carbonyl chloride as an agent for arresting isomeric change." By T. M. Lowry and E. H. Magson.

"Emulsions." By S. P. U. Pickering.

"The electrometric measurement of the hydrolysis of the salts of aniline, ammonium, aluminium, chromium, thallium, zinc, magnesium, cerium, thorium, nickel, and cobalt." By H. G. Denham.

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Issued 3/12/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 332.

Thursday, November 21st, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT announced that the Society has received a portrait of Faraday and Daniell from Professor Meldola, and a silver medal from the Société Chimique de France, struck in commemoration of the recent Jubilee celebration.

Certificates were read for the first time in favour of Messrs. :

John Arthur Carpenter, B.A., New College, Oxford.
Cyril Dickinson, B.Sc., F.I.C., Abbotsford, Holycroft Avenue, Hampstead, N.W.
Edward Mortimer Eagles, M.A., 5, Winsham Grove, Clapham Common, S.W.
Robert Cecil Gale, 38, Scarsdale Villas, Kensington, W.
George Neville Pingriff, B.A., 39, Hall Road, Handsworth, Staffs.
William Bayliss Shaw, Lonsdale House, Walsall.
Harry Jackson Unwin, Market Place, Clay Cross, nr. Chesterfield.
Herbert Walker, Whyttington, Station Road, Wealdstone, N.W.
Joseph Henry Williams, 27, Canbury Avenue, Kingston-on-Thames.

Certificates have been authorised by the Council under Bye-law I (par. 3) in favour of the following :

Edward Henry Croghan, c/o Messrs. H. Eckstein & Co., P.O. Box 149, Johannesburg.
Charles Thomas Foreman, Jamalpur, E.I.R., Bengal.

Of the following papers, those marked * were read :—

***225. "Emulsions." By Spencer Pickering.**

Paraffin oil, when churned with solutions of soap, glue, starch, albumin, &c., forms an emulsion which rises, like cream, to the surface of the excess of water, and contains from 65 to 82 per cent. by volume of the oil. Close-packing of uniform globules would give an emulsion containing 74 per cent. The percentage of oil can be increased to 99 per cent., the emulsion then being practically solid. Emulsification seems to depend on the separation from the liquid of very minute, solid particles which are attracted by, and surround, the oil globules, thus preventing them from coalescing. Any precipitated substance which is sufficiently finely divided will act as an emulsifying agent, but, after becoming agglomerated by drying, it loses this property. The basic sulphates of iron and copper are conspicuously good emulsifiers, and, when they are used instead of soap, it is possible to mix with the emulsions substances which could not be added if soap had been used; for example, sodium hydroxide. Solids which are not sufficiently fine grained to make true emulsions with oil, will sometimes made quasi-emulsions, in which the oil globules are merely entangled with the solid particles. In this case, dilution with water separates the oil from the solid, which is not the case with true emulsions.

Discussion.

Dr. Lewkowitsch thought that all the phenomena mentioned by the author could be best explained by the colloidal state of the substances employed. He would therefore take exception to the explanation that the paraffin oil emulsified the soap solution, and would prefer to say that the soap solution emulsified the paraffin oil. Soap solutions were typical colloids, easily gelatinisable even in dilute solutions, and it was also well known how disconcerting soap solutions were once they had formed an emulsion with other substances, notably vegetable or mineral oils. The percentage (97) of paraffin oil in the emulsion shown appeared very high, and he therefore asked how much water and how much soap, presumably soft soap, were in the remaining 3 per cent. Soap solutions emulsified, not only paraffin oils, but also alcohol and notably very large amounts of water.

The ferric sulphate and also the copper salt mentioned by the author were known to occur in the colloidal state, and therefore their property of forming emulsions would explain the phenomena referred to. The experiments shown with the emulsions produced by soap would fall in well with that explanation. On adding hydrochloric acid, the soap was decomposed with the formation of free fatty acids.

These, at any rate those formed in the given case, were not colloids, and therefore the emulsion was "broken" at once and water separated, the fatty acids remaining dissolved in the petroleum. The fact that caustic soda "broke" the emulsion was also easily explained, as caustic soda "salts out" soaps, that is, precipitates them from their colloidal solution, and therefore water must separate out again. That in the experiment with lime no emulsion was formed could also be readily explained by adopting his view, for under the given conditions lime would not behave like a colloid.

Mr. J. CASTELL-EVANS thought that surface-tension had a great deal, if not all, to do with the formation of emulsions, and that many finely-divided substances may be found which will induce the formation of emulsions of petroleum and water. He instanced a case, falling within his own personal observation, in an attempt at "oil concentration" of the metalliferous contents of some calcined tailings. These tailings consisted largely of ferric oxide and, after calcination, had been "weathered" for many years. On shaking up with water and mineral oil of about 0·89 sp. gr., the silicious matter, as expected, sank to the bottom of the cylinder; so also did the coarser particles of ferric oxide, whilst the finer particles of the oxide remained in the oil, forming apparently a true emulsion. This "emulsion" did not make the sides of the cylinder oily, and remained persistent for many months. The coarser particles of the oxide did not present a sufficiently large surface, in proportion to their mass, to be retained by the petroleum.

Dr. BORNS inquired whether the author had succeeded in obtaining any emulsions of oil and pure water. K. Beck (*Zeitsch. physikal. Chem.*, 1907, **58**, 409) had found that the viscosity of water was not affected when the water was churned with oil. When he prepared an emulsion of oil and water by rubbing the oil with some gum arabic in a mortar and adding water, however, the viscosity of the water was increased.

The PRESIDENT suggested that the suspended particles in an emulsion may be similarly electrified, and so repel each other and fail to coalesce. No doubt this phenomenon is closely connected with surface-tension phenomena. The addition of electrolytes may possibly discharge the electrified particles and cause coalescence.

Mr. PICKERING, in reply, stated that the strongest emulsion which he had obtained contained only 1 per cent. of a 1 per cent. soap solution. The action of soap as an emulsifying agent was very uncertain, but that was not the case with insoluble emulsifiers. Such colloids as he had tried did not emulsify, but, on the contrary, became gelatinised. The basic sulphates were clearly not colloids; the particles composing them could be seen under the microscope. No doubt surface-tension

played an important part in emulsification, but that offered no explanation of the phenomenon. Electrolytes, as such, had no effect on emulsions.

***226. "Aromatic azoimides. Part III. The naphthylazoimides and their nitro-derivatives." By Martin Onslow Forster and Hans Eduard Fierz.**

For the purpose of studying further the triazo-group, and the conditions under which its properties are influenced by other groups, azoimides of the naphthalene series have been examined.

α-Naphthylazoimide, $C_{10}H_7 \cdot N_3(\alpha)$, melts at 12°, and does not yield hydrazoic acid when heated with alcoholic potash; the 2-*nitro*- and 4-*nitro*-derivatives, melting at 103—104° and 99° respectively, are resolved into the corresponding nitronaphthols and hydrazoic acid. The heteronucleal 5-*nitro*- and 8-*nitro*-1-*naphthylazoimides*, melting at 121° and 130—131° respectively, do not furnish hydrazoic acid.

β-Naphthylazoimide, $C_{10}H_7 \cdot N_3(\beta)$, melts at 33°, and, like the heteronucleal 5-*nitro*- and 8-*nitro*-2-*naphthylazoimides*, melting at 133·5° and 108° respectively, does not give hydrazoic acid. 1-*Nitro*-2-*naphthylazoimide*, melting at 116—117°, is characterised by the readiness with which it loses nitrogen when heated, passing into the peroxide of β-naphthaquinonedioxime, which is also obtained, but less readily, from the 2-nitro-1-naphthylazoimide; the 1-nitro-2-naphthylazoimide yields hydrazoic acid when heated with alcoholic potash.

***227. "The triazo-group. Part I. Triazoacetic acid and triazoacetone (acetonylazoimide)." By Martin Onslow Forster and Hans Eduard Fierz.**

The interesting properties displayed by the triazo-group when occurring in the complex, $\begin{matrix}-CH \cdot N_3 \\ | \\ -CO\end{matrix}$, have led the authors to prepare the simplest typical compounds of this class, triazoacetic acid and triazoacetone.

Triazoacetic acid, $N_3 \cdot CH_2 \cdot CO_2H$, is a colourless substance, which crystallises in lustrous, transparent, hygroscopic plates, melting at 16°; it is a strong acid, has a faint odour recalling that of butyric acid, but much less pungent, and when dropped on a hot iron plate detonates with a moderate explosion, taking fire. The *silver* salt, $C_2H_2O_2N_3Ag$, crystallises from boiling water in lustrous, colourless needles, which decompose slowly when exposed to light; the *ethyl*

ester, $C_4H_7O_2N_3$, is a limpid, colourless oil, which boils at 45° under 2 mm. pressure, and has a very faint odour recalling chloroform rather than ethyl acetate. *Triazoacetamide*, $N_3 \cdot CH_2 \cdot CO \cdot NH_2$, crystallises from benzene in long, lustrous, colourless needles, melting at 58°.

The derivatives of triazoacetic acid are much more sluggish in their reaction with concentrated sulphuric acid than is usually the case among compounds containing the triazo-group; when shaken vigorously with the acid, however, nitrogen is liberated. A neutral solution of potassium triazoacetate may be boiled without undergoing change, but in presence of free alkali, two-thirds of the azidic nitrogen is eliminated in the elemental form, the remainder separating as ammonia.

Triazoacetone (*acetonylazoimide*), $N_3 \cdot CH_2 \cdot CO \cdot CH_3$, is a colourless, limpid oil, which boils at 54° under 2 mm. pressure; the freshly prepared substance has a very faint odour recalling that of chloroacetone, but much less pungent, spontaneously acquiring a suggestion of carbylamine after a few days. It is moderately soluble in water, and when shaken with dilute aqueous potash briskly liberates nitrogen, gas evolution being almost explosive when a 40 per cent. solution of alkali is used; dropped on a hot iron plate, the substance detonates feebly, taking fire, and concentrated sulphuric acid decomposes it immediately. The *semicarbazone*, $C_4H_8ON_6$, crystallises from hot water or absolute alcohol in long, lustrous needles, which melt without evolving gas at 152°.

The triazo-derivatives of acetone and acetic ester were prepared by the action of sodium azide on the respective chloro-compounds. The authors are engaged in a study of the products obtainable from salts of hydrazoic acid and the halogen derivatives of acids, esters, ketones, aldehydes, and alcohols.

Discussion.

Dr. Keane asked whether Dr. Forster had examined the decomposition products of the azoimides of acetic acid and ethyl acetate when two-thirds of the total nitrogen was eliminated, and if so, whether imide derivatives of the aldehydes were obtained as in the case of the camphorylazoimide?

Dr. Forster replied that these compounds were being investigated.

***228. "Studies of dynamic isomerism. Part VII. Note on the action of carbonyl chloride as an agent for arresting isomeric change." By Thomas Martin Lowry and Egbert Hockey Magson.**

Labile solutions of nitrocamphor, in which isomeric change has been suspended, have been prepared (1) accidentally by dissolving nitrocamphor in chloroform, and (2) deliberately by adding acid to the solvent chloroform. In the latter case, the solutions acquired a powerful odour of carbonyl chloride, and there can be no doubt that this is the efficient agent in arresting isomeric change in chloroform solutions.

By means of this new agent, it is possible to arrest the isomeric change of nitrocamphor in other solvents. Thus a solution in benzene and *N*/10,000 carbonyl chloride, when stored in a quartz flask, showed a change of rotatory power of only 1·4° in twenty-five days, whilst a solution to which no carbonyl chloride had been added showed a similar change in four hours. In the same way, the velocity of isomeric change in ether was reduced to one-twentieth by the addition of *N*/10,000 carbonyl chloride, but no retardation was produced by the addition of acetic anhydride to acetic acid.

***229. "The electrometric determination of the hydrolysis of salts." By Henry George Denham.**

The author has measured the hydrolysis of salt solutions with the hydrogen electrode. The *E.M.F.* of the cell, Pt_{H_2} | salt solution | saturated sol. of NH_4NO_3 | calomel electrode, was measured, and from this the concentration of the hydrogen ion was calculated.

A redetermination of the hydrolysis of solutions of aniline, chromium, and aluminium salts gave results agreeing well with those obtained by Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 193; Bruner, *ibid.*, 1900, **32**, 133; Bredig, *ibid.*, 1894, **13**, 289, and Bjerrum, *ibid.*, 1907, **59**, 336). In the case of the green chromium sulphate, the results obtained point to the conclusion that the equation given by Recoura (*Ann. Chim. Phys.*, 1895, [vii], **4**, 494) for the conversion of the blue sulphate into the green is not valid, but that the acid formed is produced through hydrolysis, and its amount depends only on the concentration and the temperature of the solution.

In the case of the salts of zinc, magnesium, thorium, cobalt, and nickel, peculiar variations in the hydrogen ion concentrations have been noticed from day to day. The most probable explanation of

this appears to be that the hydrolysis of these salts lead to heterogeneous systems, in which the second phase (hydroxide or basic salt) is present in a colloidal form.

230. "The interaction of metallic sulphates and caustic alkalis." By Spencer Pickering.

Alkalis, added to solutions of various metallic sulphates, precipitate a definite basic sulphate, except in the case of manganese and magnesium, where the hydroxide is precipitated. After the precipitation is complete, the further addition of alkali converts the basic sulphate either into another, sometimes consecutively into two other, more basic products (for example, copper and nickel), or into the hydroxide (aluminium). When one of the stronger alkalis (potash, soda) is used in excess, the product is probably always the hydroxide, but in the case of lime this does not appear to be so, at any rate not with the sulphates of copper and nickel (see the following communication). In every case examined, different alkalis have given the same results as regards the basicity of the sulphates precipitated by them in each particular case. The existence of the following eleven basic sulphates has been established in this way; the predominence of 5 as the coefficient of equivalents of metallic oxide present is very noticeable. Those marked with an asterisk are the ones formed when the whole of the metal has been precipitated from the solution; the others are products of the action of further quantities of alkali: $5NiO,3SO_3$*, $5NiO,2SO_3$, $5Al_2O_3,3\times 2SO_3$*, $4CuO,SO_3$*, $4CoO,SO_3$*, $4CdO,SO_3$*, $5CuO,SO_3$, $5NiO,SO_3$, $5ZnO,SO_3$*, $10CuO,SO_3$, $10FeO,SO_3$*.

231. "The chemistry of Bordeaux mixture." By Spencer Pickering.

The substances formed on the addition of lime to copper sulphate, as in the preparation of Bordeaux mixture, are dependent on the proportions of lime used, and may be either (1) $4CuO,SO_3,0{\cdot}06CaSO_4$; (2) $5CuO,SO_3,0{\cdot}25CaSO_4$; (3) $10CuO,SO_3,1{\cdot}3CaSO_4$; (4) $10CuO,SO_3,4CaO,SO_3$; (possibly 5) $10CuO,SO_3,10CaO,SO_3$, or (6) $CuO,3CaO$; that present in most cases probably being (4).

The fungicidal action of Bordeaux mixture seems to depend on the liberation of normal copper sulphate by the action of carbon dioxide on the basic sulphate. The action begins only after a certain lapse of time, the basic calcium sulphate having to be decomposed before the basic copper sulphate is attacked. By using only sufficient lime to

form $4CuO,SO_3$, the presence of basic calcium sulphate and the consequent delay in the action is avoided; in addition to this, the amount of normal copper sulphate liberated (for a given amount of copper sulphate taken) and the insecticidal value of the mixture will be two and a half times as great as when it consists of $10CuO,SO_3,4CaO,SO_3$.

The basic sulphates, when precipitated by lime in presence of excess of sodium sulphate, contain sodium sulphate as well as calcium sulphate; the formula of the most basic sulphate is $10CuO,SO_4,(Na_2,Ca)SO_4$. When precipitated by soda, they contain no appreciable amount of sodium sulphate, unless a large excess of the latter is present in the liquid.

Nickel sulphate with lime gives a basic sulphate containing a very little calcium sulphate, but, if the lime is at all times in excess, the basic sulphate is deprived of most of its acid, the precipitate consisting essentially of a double oxide.

232. "The alcohols of the hydroaromatic and terpene series. Part I. Resolution of the alcohols into their optically active components and the preparation of the borneols." By Robert Howson Pickard and William Oswald Littlebury.

An alternate method to that of the authors' (*Proc.*, 1906, **22**, 71) for the resolution of racemic alcohols was described. The alcohol is combined with phthalic or succinic anhydride, and the resulting acid ester resolved by *l*-menthylamine or other strong optically active base. The optically active acid ester thus obtained is readily hydrolysed and yields the active alcohol in a pure state.

l-Borneol was purified by three independent methods and found to have $[\alpha]_D$ $-37{\cdot}9°$ in toluene solution. *d*-Borneol was obtained from the reduction products of camphor by (i) treatment with zinc chloride in benzene solution, followed by (ii) conversion in the hydrogen phthalate and purification by means of the *l*-menthylamine salt. It then has $[\alpha]_D$ $+37{\cdot}8°$ in toluene solution.

*iso*Borneol (from camphene) was converted into the hydrogen phthalate and resolved by means of *l*-menthylamine and cinchonine. The *iso*bornyl hydrogen phthalates have $[\alpha]_D$ $\pm 76{\cdot}8°$ in chloroform solution, and when hydrolysed readily yield the pure *iso*borneols, which have $[\alpha]_D$ $\pm 34{\cdot}3°$ in ethyl-alcoholic solution. The identity of Haller's *iso*camphols (obtained by reduction of camphor), which had $[\alpha]_D$ $\pm 32{\cdot}9°$ in ethyl-alcoholic solution, with the inactive *iso*borneol from camphene has long been assumed. The results described may be taken as proof of this, although it is probable that the product obtained from "camphene" contains other substances besides *d*- and *l*-*iso*borneol.

233. "The electrolytic preparation of disulphides. Part I. Dibenzyldisulphide and diethyldisulphide." By Thomas Slater Price and Douglas Frank Twiss.

The electrolysis of the alkyl thiosulphates (compare *Proc.*, 1906, **22**, 260), which are used to prepare the disulphides, was originally performed in a beaker, without any diaphragm between the anode and the cathode, and the formation of disulphides was assumed to be due to the decomposition of the discharged anions, according to the equation $2R{\cdot}S_2O_3 = R_2S_2 + 2SO_3$.

Subsequent experiments, however, with divided cells, have proved the formation of disulphide to be due to the reduction of the alkyl thiosulphate anion at the cathode, according to the equation

$$2R{\cdot}S_2O_3' + 2H = R_2S_2 + 2HSO_3'.$$

The best yield of disulphide is obtained by using a low current density, a concentrated solution, and current in excess of that theoretically required; the addition of sodium carbonate or bicarbonate to the electrolyte is also advantageous.

Although the pure alkyl thiosulphate compounds were used in the earlier experiments, it has been found quite satisfactory to electrolyse the mixture obtained by heating together sodium thiosulphate and the organic halide in aqueous-alcoholic solution; a divided cell is then used.

The bearing of the above results on the constitution of sodium thiosulphate was discussed, since Gutmann, in a series of recent papers (*Ber.*, 1905, **38**, 1728 and 3276, &c.), favours the constitutional formula $\begin{matrix} S \\ O \end{matrix}\!\!>\!\!S(ONa)_2$ in place of the usually accepted formula $SO_2(ONa)(SNa)$. It was shown that the former formula is not satisfactory, and that all Gutmann's results are in accordance with the latter.

234. "The influence of solvents on the rotation of optically active compounds. Part XI. Ethyl tartrate in aliphatic halogen derivatives." By Thomas Stewart Patterson and David Thomson.

The rotation of ethyl tartrate has been determined in methylene chloride, carbon tetrachloride, ethylene chloride, ethylidene chloride, acetylene tetrachloride, bromoform, ethyl bromide, ethylene bromide, acetylene tetrabromide, methyl iodide, methylene iodide, and ethyl iodide at various temperatures and concentrations. The values found were compared with those for molecular solution-volume. To some extent an inverse relationship holds between these variables. In all the solvents under consideration, the rotation of the dissolved ethyl

tartrate is depressed below that of the homogeneous ester, whilst, on the other hand, the molecular solution-volume becomes greater than the molecular volume. Amongst the individual data also an inverse proportionality often obtains, but a correlation between the two variables cannot be traced through all the solvents examined, since exceptions are both numerous and important.

235. "The interaction in solution of ferrous sulphate and copper sulphate." By Henry Russell Ellis and William Henry Collier.

When ammonia is added to copper sulphate solution, the distinctive blue coloration is not obtained or is rendered indistinct if ferrous sulphate is present.

If excess of ferrous sulphate is present, no coloration is produced, whilst the iron is precipitated as ferrous and ferric hydroxides; the solution contains cuprous compounds, and a small quantity is present in the precipitate. The production of the ferric hydroxide is brought about by the oxidising action of the compound $CuSO_4,5NH_4OH$, and the amount of oxidation is proportional to the amount of this substance present.

Complete oxidation is brought about when both the copper and ammonia are present in excess.

The authors have been able to oxidise the whole of the iron in a few minutes in the cold by using the proportions $10NH_4OH$, $CuSO_4$, and $\frac{1}{2}FeSO_4$. Solutions of ferrous sulphate, on boiling, become hydrolysed, giving an acid solution.

No action takes place between ferrous sulphate and copper sulphate solutions in the cold, but, on boiling, the copper sulphate slowly oxidises the ferrous hydroxide produced by hydrolysis.

236. "Mercurous hyponitrite." By Edward Divers.

A paper with the above title, by P. C. Rây, published in the August number of the *Transactions*, having been taken as read, opens with the following words: "Mercurous hyponitrite, which has already been obtained in a somewhat impure condition by the author (*Trans.*, 1897, **71**, 348), may be prepared (*a*) by precipitating mercurous nitrate with carefully neutralised sodium hyponitrite made according to Divers' method (*Trans.*, 1899, **75**, 96, 119); (*b*) by precipitating mercuroso-mercuric nitrite (Rây, *Trans.*, 1902, **81**, 644) with the crude alkaline hyponitrite; or (*c*) by precipitating mercurous nitrate with acid potassium hyponitrite (Thum, *Inaug. Dissert.*, 1893)." Any

one unacquainted with the facts referred to will hardly get a correct notion of them from this obscure sentence. These facts are (1) that Thum in an unusually brilliant inaugural dissertation on hyponitrous acid gave, in 1893, a description, accompanied by excellent analyses, of the mercurous salt among others; (2) that, in 1897, there appeared a paper by Rây describing, as new, mercurous hyponitrite (in admixture with a mercuric salt) obtained from sodium hyponitrite by adding it to a solution of mercuroso-mercuric nitrite, a solution he had resort to (notwithstanding the complications likely to ensue consequent upon the presence in it of mercuric salt and upon its being a solution of a nitrite) because he supposed that mercurous nitrate would not serve for the purpose, in consequence of the acidity of its solution; and (3) that, beyond this pointless substitution of a solution of one mercurous salt for another, Rây's paper contained nothing new, nothing so good as had been already published, and yet something beneath criticism about a supposed mercuric hyponitrite (see *Trans.*, 1899, **75**, 119).

Rây's recent paper, besides implying that mercurous hyponitrite, prepared by Rây's reagent, has now been obtained free from mercuric salt in some way not even alluded to (the evidence for this being some new analyses, three out of four of which are not a whit better than those of the admittedly impure preparations), contains only the statement that this preparation of Ray's (possibly containing nitrite) cannot be dissolved in nitric acid without immediately yielding metallic mercury, notwithstanding the fact that Thum was able to reprecipitate the salt in a pure state from its solution in nitric acid, as his analysis and description establish, and that the writer (*Trans.*, 1899, **75**, 121) has published experience similar to Thum's, each working with salt of high purity.

237. "Decomposition of mercurous and silver hyponitrites by heat." By Edward Divers.

Rây and Gañguli have not succeeded in giving a definite and consistent interpretation of the results which they have recorded in their recent paper on the decomposition of mercurous and silver hyponitrites by heat (*Trans.*, 1907, **91**, 1397). They have not perceived that these results are impossible as they stand, and must be corrected if they can be. The corrections called for in the case of the silver salt lie well within the limits of errors in the experimental analyses, whilst, in the case of the mercury salt, the justifiable assumption of the presence of nitrite fairly well accounts for numbers otherwise too far from what the pure salt would have given. Had the authors been aware of the imperfect nature of their results,

in the case of the mercury salt, they would presumably have deferred publication of them. But, even as published, these results seem capable of such revision and subsequent interpretation as may make them add materially to the knowledge of the decomposition of hyponitrites by heat.

The two hyponitrites examined evidently decompose when heated each in three ways, which are expressed by the following equations. For the mercury salt, these are: $(HgON)_2 = 2Hg + 2NO$ (1); $(HgON)_2 = Hg + HgO + N_2O$ (2); $3(HgON)_2 = 4Hg + (HgNO_3)_2 + 2N_2$ (3). In Rây and Gañguli's mode of procedure, it would seem, on probable calculation, as tabulated below, that 2·96 out of 6·09 parts of the salt will have decomposed according to (1); 2·32 parts according to (2), and 0·81 part according to (3). Or, in percentage numbers, 48·6, 38, and 13·3 according to equations (1), (2), and (3) respectively.

In the case of the silver salt, where we are on much surer ground, two of the equations are just like (1) and (3) for the mercury salt, whilst the other, which only differs from (2) as given for the mercury salt because of the instability of silver oxide, is $(AgON)_2 = 2Ag + O + N_2O$ (2′), the free oxygen of which with 2NO by equation (1) becomes first N_2O_3, let us say, and then nitrite, on contact with the solution of potassium hydroxide, as Rây and Gañguli explain. Ultimately, therefore, the second equation becomes $2(AgON)_2 = 4Ag + N_2O_3 + N_2O$, but, for the sake of comparison with the mercury salt, it seems better to use the equation showing free oxygen and count the nitrite nitrogen along with that as nitric oxide. The conclusion that must be come to, after inspecting the tables, will be that Rây and Gañguli had really 7·84 (= 6·58 + 1·26) parts out of 10·15 of the silver salt decomposed according to equation (1); 1·26 parts according to (2′), and 1·05 parts according to (3) (Ag being read for Hg). Or, 83, 13·3, and 3·7 per cent. respectively according to equations (1), (2′), and (3). Reference to the authors' paper will show that they have themselves put forward equations (1) and (2), that they reject (3), and that they suggest others which, it may here be said, could not be worked in with their results in any likely way.

The interpretation, here submitted, of the effects of heating the two hyponitrites is derived from the numbers exhibited in the subjoined tables.

Distribution of the Nitrogen and Oxygen of Mercurous Hyponitrite in the Products of its Decomposition by Heat.

Product.	N_2.	N_2O.	NO.	N_2O_3.	NO_3.	HgO.	Total.	Theory.
N found ...	0·54	2·32	2·53	0·24	0·48	—	6·11	6·09
O ,, ...	—	1·33	2·89	0·41	1·65	1·19 *	7·47	6·96
N calc.	0·54	2·32	2·96	—	0·27	—	6·09	6·09
O ,, ...	—	1·33	3·38	—	0·92	1·33	6·96	6·96

Distribution of the Nitrogen and Oxygen of Silver Hyponitrite in the Products of its Decomposition by Heat.

Product.	N_2.	N_2O.	NO.	N_2O_3.	NO_3.	Total.	Theory.
N found	1·06	1·15	6·58	1·26	0·35	10·40	10·15
O ,, ...	—	0·66	7·52	2·16	1·20	11·54	11·60
N calc.....	0·70	1·26	6·58	1·26	0·35	10·15	10·15
O ,, ...	—	0·72	7·52	2·16	1·20	11·60	11·60

* See note on page 1400 in Rây and Gañguli's paper.

The numbers in the first line of each table are the mean numbers of those given by the authors for the nitrogen of the several products as parts per cent. of the salt. The column headed "N_2O_3" shows the nitrogen of the nitrite in the potassium hydroxide solution they made use of. The column "NO_3" shows the nitrogen, obtained or calculated, as mercurous or silver nitrate. In the case of the mercurous hyponitrite, the distribution of the nitrogen as nitrite and nitrate has been assumed to have been in all three experiments as 1 : 2, in agreement with what it was found to be in the only reported experiment in which it was determined by the authors.

The numbers in the second line of each table are for the oxygen corresponding with those for the nitrogen in the first line. Their sum, in the case of the mercury salt, is much in excess of the percentage of oxygen in mercurous hyponitrite. Since the mercurous hyponitrite, which the authors made use of, had been prepared from mercuroso-mercuric nitrite, the excess of oxygen found may be attributed to the presence of nitrite in the salt as prepared. The column headed, HgO, shows the oxygen left as mercuric oxide as being necessarily equal to that in the nitrous oxide, less (in the second line) by one-third of that as nitrous anhydride (1·33—0·14 = 1·19).

The numbers in the third and fourth lines of each table have been calculated in accordance with the equations already given, and in such a way as to make them differ the least possible from the numbers furnished by the experiments, under the necessary condition that their respective sums shall be identical with the percentages of nitrogen and oxygen in the pure mercurous and silver hyponitrites. In the case of the mercury salt, it has been assumed that, when free

from nitrite, mercurous hyponitrite yields no red fumes and very little nitrate, which is in accordance with the writer's experience, referred to by the authors. The numbers for the silver salt have been altered to make the free nitrogen equal to only twice that found as nitrate; that found as nitrous oxide to be equal to that as nitrite, and total nitrogen and oxygen to be equal respectively to the percentages of these elements in the pure salt.

A noticeable point in Rây and Gañguli's paper is their experience of the conversion by heat of nearly one-eighth of silver hyponitrite into silver, nitrous oxide, and oxygen. The writer did not observe the presence of any nitrous oxide in his experiments (*Trans.*, 1899, **75**, 108). Nor has any other worker recorded the fact of having done so. On the evidence afforded by Rây and Gañguli's experiments, the writer is prepared to admit that nitrous oxide may never be absent altogether in the products of the decomposition of silver hyponitrite by heat. As to the matter of quantity of nitrous oxide, the details of their experiments and his are sufficiently different to account for the fact of their obtaining so much of it and he so little as to pass unnoticed. The salt they used contained, they think, impurities enough to be mentioned, and began to decompose very slowly at 100°, and at 140° suffered rapid decomposition. It had been dried cold over sulphuric acid under reduced pressure, but was heated to decomposition in a tube between which and the Sprengel pump a tube of "aqueous potash" intervened. A very little moisture would have given a lower temperature of decomposition, and caused free generation of nitrous oxide. In the writer's experiments, salt of high purity, dried finally in a Sprengel vacuum at 98°, was used. Thus dried, the pure salt hardly begins to decompose at 140°, and is not in free decomposition much, if at all, below 160°. It would seem highly probable from the difference in the effects of heat that the generation of nitrous oxide is largely, if not wholly, a matter of hydrolysis.

Another point worthy of attention in Rây and Gañguli's paper is their contention that nitric peroxide is a secondary product arising out of the union of nitric oxide with the oxygen set free along with nitrous oxide. The writer thinks this to be highly probable. His position as to nitric oxide and nitric peroxide being primary products has been that for twenty years, he held, without proof, that nitric oxide was the primary product which produced red fumes by contact with air. Thum proved, in 1893, that out of contact with air the salt still gave nitric peroxide when heated. The writer then examined the matter himself for the first time and found Thum right. Having ascertained that nitric peroxide and silver gave silver nitrate and nitric oxide, he concluded, in 1899, that nitric peroxide was the primary

product and nitric oxide secondary. Now he returns to his first view and agrees with Rây and Gañguli that nitric oxide is the primary product, at the same time being certain that it is also reproduced by reduction of the nitric peroxide by silver.

It is much to be desired that Rây and Gañguli would repeat their experiments, making use of pure mercurous hyponitrite prepared by Thum and the writer's process, and of the driest pure silver hyponitrite, in their apparatus supplied with some solid potassium hydroxide in the near end of their absorption tube.

238. "Cupric nitrite." By Edward Divers.

A paper appeared not long ago in the *Transactions* (1907, 91, 1405) on cupric nitrite, in which Rây sets forth his observations on what he regards as being the atmospheric oxidation and autoxidation of this salt. Now nitrites, as such, do not oxidise and, in the cases where they do not hydrolyse in water, they are stable in solution. (The passage of cobaltous into cobaltic nitrite is, of course, no exception to the statement.) What Rây has occupied himself with is simply the oxidation of nitrous acid, not cupric nitrite, in aqueous solution. For when a cupric salt is dissolved in water, it is always hydrolysed to some extent, as is shown by its acid reaction and other facts. Nitrous acid in aqueous solution becomes nitric acid and nitric oxide, and nitric oxide oxidises in the air. When it is added that nitric acid decomposes some of the cupric nitrite to form nitrate together with more free nitrous acid, there seems to be no more to be said. As to the oxidation of cupric nitrite, as such, we are left as we were, without any evidence whatever of its occurrence.

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—— Radiation from, and melting points of, palladium and platinum. (From the *Bull. Bureau of Standards, Washington*, 3, 1907.)

RESEARCH FUND.

A Meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, December 9th, 1907.

All persons who received grants in December, 1906, or in December of any previous year whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, December 2nd, next.

At the next Ordinary Meeting, on **Thursday**, December **5**th, 1907, at **8.30** p.m., there will be a ballot for the election of Fellows, and the following papers will be communicated :

"The affinity constants of bases as determined by the aid of methyl-orange." (Preliminary note.) By V. H. Veley.

"The velocity of reduction of the oxides of lead, cadmium, and bismuth by carbon monoxide, and the existence of the suboxides of these metals." By F. J. Brislee.

"The relation between unsaturation and optical activity. Part I. The menthyl and bornyl esters of β-phenylpropionic, cinnamic, and phenylpropiolic acids." By T. P. Hilditch.

"The constituents of the essential oil of nutmeg." By F. B. Power and A. H. Salway.

"Methyl ethers of some hydroxyanthraquinones." By A. G. Perkin.

"The colouring matters of the stilbene group. Part IV. The action of caustic alkalis on paranitrotoluene and its derivatives." By A. G. Green, A. H. Davies, and R. S. Horsfall.

"The replacement of alkyl radicles by methyl in substituted ammonium compounds." By H. O. Jones and J. R. Hill.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 5th, 1907.

Banks, Arthur John,

61, Lawton Road, Waterloo, Liverpool.

Research Chemist. Studied Theoretical and Practical Chemistry and Microscopy in the laboratory of the late A. Norman Tate, F.I.C., F.C.S., 7–11, Hackins Hey, Liverpool (1881-2-3-4); have since been continuously engaged in analytical and research work; the past 4½ years (1902–7) have been devoted to an enquiry into the factors governing the "strength and other qualities" of wheat. Contributions: "Note on the Laboratory Drying Oven," *Chem. News*, 58, 54 (1888). Note on "A New Chemical Test for Strength in Wheat," *Nature*, 75, 460—1 (1907). Collaborated with F. W. Fellowes in the preparation of the following papers, viz.: (1) "Some of the Micro-organisms Causing the Diseases of Beer," *Trans., North of England Institute of Technical Brewing*, 3, 107—136 (1894), on p. 129 reference is made to my apparatus for cultivating anaërobic organisms by means of plate growths; (2) "Facts, Fancies, and Fallacies," *Trans. of the Federated Institutes of Brewing*, 2, 247—272 (1896). Further reference to my work was made by Alf. Jörgensen in his paper "Hansen's System of Pure Yeast Culture in English Top Fermentation," *Trans., Institute of Brewing*, 7, 235, 246 (1894).

Horace T. Brown. W. J. Cousins.
Arthur R. Ling. *Francis Henry Tate.*
George T. Holloway.

Barnett, Edward de Barry,

40, Queensborough Terrace, Hyde Park, W.

Research Student, University College, London.

William Ramsay. J. Norman Collie.
R. W. Gray. Edward C. Cyril Baly.
B. D. Porritt.

Bell, John Forbes,

Craigmillar, Edinburgh.

Brewer's Chemist. Bronze Medallist and First Class Honours Certificate in Brewing, City and London Guilds Institute. Studied Chemistry under Mr. John Hunter, F.I.C., F.C.S., Analyst for County of Midlothian, &c. Member of Committee of the Scottish Section of the Institute of Brewing.

John Hunter. John S. Ford.
Matthew J. Cannon. John M. Guthrie.
John Doull.

Buckney, Frank,

51, Highbury Park, London, N.

Demonstrator in Cambridge University Laboratory. Honours in Chemistry, Tripos Parts I. and II. Cambridge. Original research: "A New Optically Active Tetrahydroquinoline Compound," delivered before Cambridge Philosophical Society.

F. H. Neville. H. O. Jones.
W. J. Sell. F. E. E. Lamplough.
J. Parkin. F. W. Dootson.

Callan, Thomas,

22, Church Street, Egremont, Cheshire,

Research Chemist. Assistant Chemist to Messrs. J. Woolley, Sons, and Co., Manchester, 1900–3. B.Sc., Victoria University of Manchester, with First Class Honours in Chemistry, 1906. Am now Research Assistant to Prof. J. Campbell Brown, Liverpool University.

J. Campbell Brown. D. L. Chapman.
A. W. Titherley. H. B. Dixon.
J. F. Thorpe.

Caton, Frederic William,

6, King Street, Snow Hill, E.C.

Research Chemist at Wellcome Chemical Research Laboratories. B.A. (Oxford), B.Sc. (London). Have spent one year in Research in Mr. J. E. Marsh's Laboratories at Oxford.

Frederick B. Power. J. E. Marsh.
John Watts. W. W. Fisher.
Allan F. Walden. R. de J. Fleming-Struthers.

Crisp, George Hugh,

62, Gainsboro' Road, Crewe.

Chemistry Master at the Cheshire County School, Crewe. B.A.

(Oxon.); Third Class Honours in Natural Science (main subject: Chemistry). Wishes to keep in touch with recent researches in Chemistry.

N. V. Sidgwick. H. B. Hartley.
A. F. Walden. A. Angel.
D. H. Nagel. *H. Brereton Baker.*

Day, Edward Joseph,
Dorchester.

Doctor of Medicine (Durham University). Medical Officer of Health (Rural and Urban), Dorchester Borough and Dorchester Rural Sanitary District. Over twenty years both appointments. M.D. (Durham); M.R.C.S. (England); L.S.A. (London). Late Public Analyst for Boroughs of Dorchester, Bridport, and Lyme Regis.

John Hunter. Fredk. Hudson-Cox.
A. H. M. Muter. Edward Russell.
Chas. J. Waterfall.

Dupré, Frederick Harold,
Mount Edgcumbe, Sutton, Surrey. Business address: 2, Edinburgh Mansions, Howick Place, S.W.

Analytical and Consulting Chemist. Ten years Assistant to the late Dr. A. Dupré, F.R.S. At present, jointly with my brother, P. V. Dupré, Acting Chemical Adviser to the Explosives Department of the Home Office.

Otto Hehner. Bernard Dyer.
W. J. Dibdin. Henry E. Armstrong.
Gerald T. Moody.

Dupré, Percy Vivian,
Mount Edgcumbe, Sutton, Surrey.

Analytical and Consulting Chemist. Associate of the City and Guilds of London Institute. Eight years' work under the late Dr. Dupré, F.R.S. Have had two papers published in the *Analyst* (Aug., 1905, and July, 1906). Acting Chemical Adviser to the Explosives Department of the Home Office in conjunction with my brother.

Otto Hehner. Bernard Dyer.
W. J. Dibdin. Henry E. Armstrong.
Gerald T. Moody.

Dutton, Francis Bridger,
Birch Hall, Windlesham, Surrey.
Student in Chemistry, Oxford, Magdalen College.

A. F. Walden. D. H. Nagel.
N. V. Sidgwick. T. S. Moore.
H. B. Hartley.

Fawcitt, Claude Scott,

Darlington, England, and Shimoga, S.M. Ry., India.

Analytical Chemist. Undergraduate of Durham University. Seven years in laboratory of Messrs. J. and H. S. Pattinson, Newcastle-on-Tyne. Three years Chemist at Messrs. The Vizianagram Mining Coy.'s Manganese Mines, and at present Analyst to The Mysore Manganese Coy., Ltd.

A. W. Comber. J. T. Dunn.
John Pattinson. P. Phillips Bedson.

F. C. Garrett.

Greenough, Thomas Rigby,

Beechwood, Leigh, Lancashire.

Graduate of University of Cambridge (Natural Science Tripos, 1907). Analytical Chemist under Sir Charles Cameron, Dublin. Worked three years in Caius College Laboratory, Cambridge, under M. M. Pattison Muir.

M. M. Pattison Muir. Percy Bean.
W. H. Leek. Frank Scudder.
Charles T. Heycock. *Robert Pettigrew.*

Hay, William,

Holton House, Beverley Road, Hull.

Student in the Research Laboratory of the Pharmaceutical Society. "Minor" and "Major" examinations of the Pharmaceutical Society.

Arthur W. Crossley. F. Filmer De Morgan.
E. Towyn Jones. W. Palmer Wynne.

M. O. Forster.

Hutchinson, William Doge,

Lythmore, Tennyson Road, Harpenden, Herts.

Engaged in Research at Rothamsted Experimental Station. Second Class Honours in Chemistry at Oxford.

A. D. Hall. D. H. Nagel.
N. H. J. Miller. H. B. Hartley.

R. T. Lattey.

Ingham, Harry,

26, Hamilton St. Bury, Lancs.

Lecturer at the Technical School, Bury. Master of Science (Vict.). Contributed to the "Transactions of the C.S., 1907, Vol. **91**," in conjunction with Dr. J. F. Thorpe and Dr. E. F. J. Atkinson, a paper

on the "Formation and Reactions of Imino-compounds. Pt. III." I wish to keep in touch with the progress of Chemical Research.

W. H. Perkin, jun. — Norman Smith.
J. F. Thorpe. — J. C. Cain.
William Dixon.

Jones, Benjamin Owen,
Boksburg, Transvaal.

Chemist (M.P.S., Gt. Britain). Member of the Legislative Assembly, Transvaal. Member of the Transvaal Pharmacy Board (Government Nominee). Examiner in Pharmacy to above Board. Member and Vice-Chairman of Rand Provisional Joint Committee (Hospitals) and Chairman of East Rand Hospitals (Witwatersrand).

M. Carteighe. — Peter MacEwan.
J. Rymer Young. — John C. Hewlett.
E. J. Millard.

Kaye, John,
Westerfield, Perth.

Research Chemist (on Glass in N.B. Glass Works, Perth). M.A., B.Sc. (Glasgow) in Pure Science. Chemistry taken both in First and Final Examinations. Acted as Demonstrator in Senior Laboratory (Glasgow University). Eighteen months' research on "Optically Active Compounds." Two papers published on "Optical Superposition," *Trans. of Chem. Soc.*, 1906, Vol. 89; 1907, Vol. 91.

T. S. Patterson. — Charles E. Fawsitt.
Frederick Soddy. — Thomas Gray.
John Ferguson.

Marsden, Herbert,
Bramford, Ipswich.

Chemist. B.Sc., Manchester. Assisted Prof. Kipping during the past 12 months in his work on "Organic Silicon Compounds." Chemist at Messrs. Packard & Co.'s Agricultural Works, Ipswich.

Harold B. Dixon. — W. H. Perkin, jun.
F. Stanley Kipping. — J. L. Simonsen.
R. M. Caven. — Francis Jones.

Marshall, Hubert Frederick Sankey,
High Street, Burwell, Cambs.

Analyst. Pupil to E. M. Chaplin, Esq., Ph.D., two years. Student Wakefield and Glo'ster Technical Schools, three years. Junior Analyst to Messrs. Stephenson's, Ltd., Cement Works, Burwell. Now Chemist-in-Charge to Messrs. Stephenson.

Edward M. Chaplin. — George Embrey.
Robert Stephenson. — *J. M. Collett.*
Jack V. J. Hayman. — *Robert J. Caldwell.*

Martin, Gerald Hargrave,

Delce, Park Rd., Wallington, Surrey.

Wholesale Optician's Assistant. Chemical Student, Birkbeck College.

Alex. McKenzie.	George W. Clough.
W. G. Tonner.	Henry Wren.

H. F. C. Goltz.

Moore, John Edward Langford,

Walton Cottage, Loughboro' Park, S.W.

Head Dispenser to St. Bartholomew's Hospital, E.C. Teacher of Practical Pharmacy and Demonstrator in Materia Medica to St. Bartholomew's Hospital Medical School. Member of the Pharmaceutical Society. My desire for Fellowship arises from my wish to have access to the Society's Library and Literature and to keep myself in touch with advanced chemical knowledge.

F. D. Chattaway.	J. A. Ormerod.
W. H. Hurtley.	W. L. Howie.
Kenneth S. Caldwell.	*W. J. Russell.*

Mummery, Charles Samuel,

Christ's Hospital, West Horsham.

Undergraduate of London University, and at present engaged in advanced experimental work in Chemistry. Is desirous of being in a position to attend the Scientific Meetings of the Society, and also of receiving the Society's Journal and Proceedings.

Henry E. Armstrong.	Chas. E. Browne.
Gerald T. Moody.	W. A. Davis.
T. H. Boardman.	*William Robertson.*

Saunders, George Joseph,

School of Mines, Charters Towers, Queensland, Australia.

Demonstrator and Assistant Lecturer in Chemistry, Assaying, and Metallurgy, School of Mines, Charters Towers, Queensland. Three years Student in Chemical and Metallurgical Laboratories, University of Sydney, N.S.W. Graduated as B.E. (Mining and Metallurgy), 1904, Syd. Univ. Eight months Assaying and Manager of Cyanide Works, Nil Desperandum Gold Mine, Forbes, N.S.W. Nine months Assaying, Mt. Eurow Copper Mine, N.S.W. One month Assaying, North Lachlan Gold Mine, Forbes, N.S.W.

J. A. Schofield.	Charles Walker.
Basil Turner.	A. Liversidge.

George Harker.

Smith, Robert Harry,

Apsley House, Priory Road, Sheffield.

Undertaking private analysis and research. Science Teacher, holding South Kensington (Science and Art Department) Certificates in Inorganic and Organic Chemistry. Trained at the Royal College of Chemistry, London.

Frank Clowes. G. T. W. Newsholme.
W. Gowland. *J. H. Coste.*
Wm. Jno. Livingston.

Stobie, Harold Ramsay,

"Clovelly," Craighall Gardens, Edinburgh.

Analytical Chemist. Certificates in Physics and Chemistry (Part I) of the Heriot-Watt College, Edinburgh. Certificate for the complete course of Chemistry and Allied Subjects of the Royal College of Science, Kensington, S.W.

James C. Philip. H. E. Fierz.
M. O. Forster. G. T. Morgan.
Chapman Jones.

Thomas, Frederick, B.Sc.,

29, Fairhaven Road, St. Anne's-on-the-Sea, Lancs.

Assistant Research Chemist. Hons. in Chemistry, University of Manchester, 1906. Research Student till March, 1907. Joint author, with Drs. Bentley, Friedl, and Weizmann, of "Derivatives of Naphthacenequinone" (*Trans.*, 1907, **91**, 411). Since March, 1907, Research Assistant to Messrs. A. G. Perkin and W. P. Bloxam at Leeds University for Research on Indigo under the Government of India.

H. B. Dixon. Norman Smith.
W. H. Perkin, jun. A. G. Green.
J. F. Thorpe. A. G. Perkin.
W. P. Bloxam.

Timpany, Harold Munkman,

St. Winifrede's Gardens, Shrewsbury.

Principal, Technical Schools, Shrewsbury. M.Sc. (Vict.). Principal of, and Lecturer in Chemistry at, Shrewsbury Technical Schools. Author of following School Text-Books: "Arithmetic of Chemistry and Physics" (Blackie); "Qualitative Analysis Tables with Equations and Notes" (Blackwood).

H. B. Dixon. Norman Smith.
G. H. Bailey. J. F. Thorpe.
D. L. Chapman.

Watson, George Arthur,

7, Roseneath Villas, Cork.

Chemistry Lecturer, Co. Cork Technical Instruction Committee. Consulting Chemist. Associate of Royal College of Science, Faculty of Applied Chemistry. Teacher of Chemistry, Cork Grammar School.

W. N. Hartley. H. M. Atkinson.
James H. Pollok. Jno. Northing.
A. J. O'Farrelly. *P. Bertram Foy.*

Wechsler, Marcus,

136, Sinclair Road, Kensington, W.

Analytical Chemist. D.Sc., Grenoble (France). Contribution to "The Study of Acenaphthene" (Dissertation, Grenoble, December, 1906). Contribution to Th. Zincke's "Method for Condensing Hydrocarbons with Benzylchloride" (Dissertation, Grenoble, December, 1906). "The Constitution of Benzylacenaphthene" (*Bull. Soc. Chim.*, (3e) T. 31–32, p. 922). At present engaged on Analytical and Research Work at Gillman and Spencer, London.

Alex. McKenzie. G. W. Clough.
Henry Wren. H. B. P. Humphries.
W. G. Tonner.

Wheeler, Edward,

113, Highbury Quadrant, London, N.

Assistant in Chemical Dept., at Central Technical College, South Kensington. Associate of the City and Guilds Institute (A.C.G.I.) in Chemical Dept.

Henry E. Armstrong. William A. Davis.
William Robertson. Edward Horton.
T. Martin Lowry. *John Vargas Eyre.*
Walter H. Glover.

Whymper, Robert,

St. Clare, St. Mary's Road, Ditton Hill, Surrey.

Research Chemist. Associate of City and Guilds Institute. Salters' Coy.'s Research Fellow.

Henry E. Armstrong. Robert J. Caldwell.
Wm. Robertson William A. Davis.
John Vargas Eyre. Edward Horton.

Williams, Percy,

c/o The Wilhelmina Co., Pontianak, Dutch West Borneo.

Chemist. B.Sc., London. "The Borides of Calcium, Strontium, and Barium," in collaboration with H. Moissan (*C.R.*, 1897). Two papers on "Double Carbides" (*C.R.*, 1898). "The Transition Point of Schömt," in collaboration with Prof. van't Hoff. "The Hydrates of

Manganese Chloride," in collaboration with H. M. Dawson (*Zeit. Phy. Chem.*, 1899). "A New Method for the Determination of Transition Points," in collaboration with H. M. Dawson (*Amer. Jour. Phy. Chem.*, 1899). 1900–1906, Chemist to the "British Uralite" Company, Higham, Kent. 1906, Chemist to the "Wilhelmina" Co., Pontianak, Dutch West Borneo.

William Ramsay. J. Norman Collie.
Frank Collingridge. N. T. M. Wilsmore.
G. Nevill Huntly. Samuel Smiles.

Noël Heaton.

Willott, David, B.Sc.,

Rosedale, Thorncroft Road, Sutton, Surrey.

Science Lecturer. Was a student of Chemistry at the Manchester Technical School, and afterwards at the South-Western Polytechnic, Chelsea. Have been a lecturer in Chemistry for 15 years at the Swansea Municipal Technical School, the Sutton Technical School, &c. Took the B.Sc. Degree of the London University with Honours in Chemistry. I wish to become a Fellow of the Chemical Society that I may keep in touch with current chemical literature.

F. H. Lowe. J. C. Crocker.
Sidney Skinner, *John Wilson.*

J. L. White.

Wilson, William John,

28, Windmill Street, Gravesend, Kent.

Analytical Chemist. Associate of the City and Guilds of London Institute. Assistant Chemist to the Associated Portland Cement Manufacturers (1900), Ltd.

Henry E. Armstrong. Edward Horton.
William Robertson. W. A. Davis.

Gerald T. Moody.

Wootton, Hubert Arthur, B.A. (Cantab.), B.Sc. (Lond.).

20, Great College Street, Westminster.

Science Master in Westminster School. Formerly Assistant Demonstrator in the University Chemical Laboratory, Cambridge. Formerly Assistant Lecturer of Clare College, Cambridge.

W. J. Sell. H. J. H. Fenton.
T. B. Wood. H. O. Jones.

H. Brereton Baker.

The following certificates have been authorised by the Council for presentation to Ballot, under Bye-law I (3):

Croghan, Edward Henry,

c/o Messrs. H. Eckstein & Co., P.O. Box 149, Johannesburg.

Analytical Chemist. Matriculation and full chemical course at the South African College, Cape Town, from 1899—1902. Also Laboratory Assistant to Professor Hohn for 2 years. 1903—1906, Assistant Analytical Chemist to Messrs. H. Eckstein & Co. At present, Chief Chemist to this firm. I have written *two* papers for the Chemical, Metallurgical, and Mining Society of South Africa, and *one* for the British Association at their meeting in South Africa. I wish to keep in touch with Chemical progress.

James Moir. J. McCrae.

Foreman, Charles Thomas,

Jamalpur, E.I.R., Bengal, India.

(Chief) Chemist and Metallurgist to the East Indian Railway. From March, 1887, to Dec., 1899, Assistant Chemist to the Consett Iron and Steel Co., Durham.

Paul Brühl. *W. R. Criper.*
David Hooper. *W. T. Grice.*

Schober, William Bush,

Lehigh University, South Bethlehem, Pa., U.S.A.

Professor of Chemistry. B.Sci., 1886; A.M., 1890, St. John's College, Annapolis, Maryland. Ph.D., Johns Hopkins University, 1892. Instructor in Chemistry, Lehigh University, 1892—1902; Assistant Professor, 1902—1906; Professor, 1906.

Ira Remsen. Chas. H. Herty.
Chas. B. Dudley. *Chas. Baskerville.*
Marston T. Bogert.

R. CLAY AND SONS, LTD., BREAD ST. HILL, E.C., AND BUNGAY, SUFFOLK.

Issued 13/12/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. No. 333.

Thursday, December 5th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The PRESIDENT announced that Professor Wislicenus, of Tübingen, was arranging to establish a memorial to the late Professor Lothar Meyer.

Certificates were read for the first time in favour of Messrs. :

Edward Philip Andreae, Ph.D., Crestalba, Champion Hill, S.E.
Marie Joseph Arsène Braun, Ph.D., 5, Aspinall Road, Brockley, S.E.
William Henry Collier, 13, Powis Gardens, Bayswater, W.
John Maxwell Heron, North House, Manningtree, Essex.
Thomas Percy Hilditch, 4, Park Hall Place, E. Finchley, N.
Capet Darcy Morewood, Ferndale, Frodingham, Doncaster.
Alfred William Oke, B.A., LL.M., 32, Denmark Villas Hove.
Douglas Robert Pinnoik, 31, The Gardens, E. Dulwich, S.E.
Arthur Robert Runeekles, 68, Kyrle Road, New Wandsworth, S.W.
Adolph Octavius Trechmann, The Old Palace, Rochester.
Alfred Wade, Government Pharmacist, Fiji.
Herbert Edmeston Watson, B.Sc., Tringhurst, Cranes Park, Surbiton.
Harry Percy Wilson, 3, Audley Road, Colchester.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:

Arthur John Banks.
Edward De Barry Barnett.
John Forbes Bell.
Frank Buckney, B.A.
Thomas Callan, B.Sc.
Frederic William Caton, B.A., B.Sc.
George Hugh Crisp, B.A.
Edward Henry Croghan.
Edward Joseph Day, M.D., M.R.C.S.
Frederick Harold Dupré.
Percy Vivian Dupré.
Francis Bridger Dutton.
Claude Scott Fawcitt.
Charles Thomas Foreman.
Thomas Rigby Greenough, B.A.
William Hay.
William Doge Hutchinson, B.A.
Harry Ingham, M.Sc.
Benjamin Owen Jones.
John Kaye, M.A., B.Sc.
Herbert Marsden, B.Sc.
Hubert Frederick Saukey Marshall.
Gerald Hargrave Martin.
John Edward Langford Moore.
Charles Samuel Mummery.
George Joseph Saunders, B.E.
William Bush Schober, A.M., B.Sci., Ph.D.
Robert Harry Smith.
Harold Ramsay Stobie.
Frederick Thomas, B.Sc.
Harold Munkman Timpany, M.Sc.
George Arthur Watson.
Marcus Wechsler, D.Sc.
Edward Wheeler.
Robert Whymper,
Percy Williams, B.Sc.
David Willott, B.Sc.
William John Wilson.
Hubert Arthur Wootton, B.A., B.Sc.

Of the following papers, those marked * were read:—

***239. "The affinity constants of bases as determined by the aid of methyl-orange." (Preliminary note.) By Victor Herbert Veley.**

In a former communication (*Trans.*, 1907, **91**, 155), it was shown that if x be the units of 0·1 c.c. hydrochloric acid added to an $N/40{,}000$ solution of methyl-orange, and y be the heights of a variable tintometer column, expressed in centimetres, required to produce the required match in tint, then $y = kx - b$. In this expression, k is the essential factor (or constant) of y in terms of x and b is accidental.

Certain values of k were obtained for hydrochloric acid, as also for the hydrochlorides of some aminocarboxylic acids.

As it was thought that such values might serve to determine the amount of free hydrochloric acid, and hence the degree of hydrolysis of the hydrochlorides of bases, preliminary experiments were made without any special care with a sample of *m*-phenylenediamine hydrochloride. It was then found with aqueous solutions of this salt containing an equi-acidic quantity of this acid, whether free or combined, that the ratio $k[\frac{1}{2}C_6H_4(NH_2)_2,2HCl]/k[HCl] = 0{\cdot}5$ approximately. In other words, 50 per cent. of the salt is hydrolysed into the free base and acid. As the result is identical with that obtained by Bredig

(*Zeitsch. physikal. Chem.*, 1894, **13**, 214), it was thought that this very simple line of investigation might be pursued further. So far, the hydrochlorides of about 40 bases of various degree of complexity, ranging from hydroxylamine to cinchonidine, have been examined. Several results are found to be in accordance with the expression of Arrhenius, $k_b/k_w = (1-x)v/x^2$ (*Zeitsch. physikal. Chem.*, 1881, **5**, 17), even at the great dilutions examined, whilst in the case of bases of analogous composition the ratio of the hydrolysis values found is nearly equal to the ratio of the heats of neutralisation with hydrochloric acid.

*240. "The constituents of the essential oil of nutmeg." By Frederick Belding Power and Arthur Henry Salway.

The material employed in this investigation consisted of an oil which was distilled from unlimed Ceylon nutmegs of good quality, and was obtained in a yield of 6·94 per cent. It had $d\ 15°/15° = 0·8690$; $a_D + 38°4'$ in a 1-dcm. tube; acid value, 0·81; ester value, 3·15. The more complete examination of the oxygenated constituents of the oil was accomplished by means of a product, designated heavy oil of nutmeg, from which the terpenes had been to a large extent removed. This had $d\ 20°/20° = 1·102$; $a_D + 1°17'$ in a 1-dcm. tube; saponification value, 6·10.

This investigation has shown that the essential oil of nutmeg contains the following substances: (1) eugenol and (2) *iso*eugenol (about 0·2 per cent.); (3) *d*-pinene and (4) *d*-camphene (about 80 per cent.); (5) dipentene (about 8 per cent.); (6) *d*-linalool, (7) *d*-borneol, (8) *i*-terpineol, and (9) geraniol (about 6 per cent.); (10) a new *alcohol*, yielding on oxidation a *diketone*, $C_8H_{14}O_2$ (a very small amount); (11) a trace of an *aldehyde* resembling citral, but yielding a *β-naphthacinchoninic acid* derivative melting at 248°; (12) safrole (about 0·6 per cent.); (13) myristicin, $C_{11}H_{12}O_3$ (about 4 per cent.); (14) myristic acid, in a free state (about 0·3 per cent.), and apparently a small amount in the form of esters; (15) formic, acetic, butyric, and octoic acids, and a new *monocarboxylic acid*, $C_{13}H_{18}O_3$, all in the form of esters, and in relatively small amount.

This investigation has also shown that the portion of nutmeg oil which has hitherto been designated "myristicol" is a mixture of alcohols, of which terpineol appears to be the predominating constituent.

Discussion.

Dr. Wade remarked that none of the constituents which had been isolated seemed to possess the characteristic odour of nutmeg, and

asked whether the authors had been able to trace this odour to its source.

Dr. POWER stated that the characteristic odour of nutmeg oil is not that of any individual substance, but is due to the mixture of odorous compounds contained in the oil.

***241. "The resolution of *sec.*-octyl alcohol (methylhexylcarbinol. Octane-2-ol)." By Robert Howson Pickard and Joseph Kenyon.**

sec.-Octyl alcohol is readily converted into the acid phthalic ester. The dextro-sec.-*octyl hydrogen phthalate* is then obtained by the fractional crystallisation of its *brucine* salt from acetone, and the corresponding *lævo*-compound by the fractional crystallisation of the *cinchonidine* salt from aqueous acetone.

The *sec.*-octyl hydrogen phthalates have $[\alpha]_D$ 48·2° in ethyl-alcoholic solution, and when hydrolysed yield the pure alcohols which have $[\alpha]_D^{17}$ 9·87°.

242. "The velocity of reduction of the oxides of lead, cadmium, and bismuth by carbon monoxide, and the existence of the sub-oxides of these metals." By Francis Joseph Brislee.

The production of lead, cadmium, and bismuth suboxides by the reduction of the higher oxides with carbon monoxide has been investigated. The velocity of reduction of the oxides was determined by heating the oxides, contained in a porcelain boat, to 300° in an apparatus in which carbon monoxide was circulated. The boat was withdrawn from time to time and the loss in weight observed. The time interval varied from one and a half to six hours. The results were then plotted as time-reduction curves, and these showed a distinct break at the point at which the analytical composition of the product was near that required for the suboxide. The position of the break was not always at the suboxide point, the position depending on the relative velocities of the two reductions, namely:

(1) Oxide $\longrightarrow$ suboxide.
(2) Suboxide $\longrightarrow$ metal.

When the velocity of (1) is very different from (2), then the break will occur at the point when the oxide is entirely reduced to suboxide. When these two velocities are not very different, the first stage of the reduction is

(1*a*) Oxide $\longrightarrow$ suboxide $\longrightarrow$ metal,

and the second is:

(2*a*) Suboxide —> metal,

and then the break will occur below the point, corresponding to complete reduction of the oxide to suboxide. The experiments made on the velocity of reduction of the oxides of lead, cadmium, and bismuth confirm Tanatar's results (*Zeitsch. anorg. Chem.*, 1901, **27**, 304) that the suboxides of these metals are definite chemical compounds, but do not prove the stability of these compounds. The suboxides of lead, cadmium, and bismuth are formed as intermediate phases in the reduction of the oxide to metal by carbon monoxide.

243. "The relation between unsaturation and optical activity. Part I. The menthyl and bornyl esters of β-phenylpropionic, cinnamic, and phenylpropiolic acids." By Thomas Percy Hilditch.

In order to throw further light on Walden's statement that increase of unsaturation in a compound is accompanied by increase in rotatory power, the author has prepared and investigated the properties of the menthyl and bornyl esters of the above three acids. Menthyl hydrocinnamate (m. p. 28°), menthyl phenylpropiolate (m. p. 33°), and bornyl phenylpropiolate (m. p. 45°) were obtained as nearly colourless, crystalline solids, whilst the other three esters were found to be liquid at the ordinary temperature. The boiling points of the compounds, as well as the specific gravities, seem to show a regular increase with increase of unsaturation, whilst the refractive indices rise with a change to an ethylenic linking, but fall to an intermediate value for the further change to an acetylenic compound.

The following conclusions were arrived at as regards optical activity:

(1) The change in rotation for either change of constitution is relatively small.

(2) The changes are nevertheless perfectly definite, and occur in a regular manner for corresponding stages of unsaturation (the rotations being measured at three successive concentrations in each of two solvents, chloroform and acetone).

(3) The conversion of a saturated to an ethylenic bond is accompanied by an increase in optical activity, whilst the change from a saturated to an acetylenic linking produces a decrease in rotatory power.

(4) In the case of esters, the change in rotation must be measured with reference to the difference between the specific rotation of the ester and that of the active alcohol from which it was formed.

(5) Walden's results are confirmed so far as the change to an ethylenic linking is concerned, but there is a discrepancy with regard to the influence of the triple bond on the optical activity.

244. "Methyl ethers of some hydroxyanthraquinones." By Arthur George Perkin.

The author has re-examined the principal non-tinctorial derivatives of anthraquinone present in Chay-root, *Oldenlandia umbellata* (Perkin and Hummel, *Trans.*, 1893, **63**, 1160, and 1895, **67**, 817), and finds, contrary to the suggestion of Böck (*Monatsh.*, 1902, **23**, 1008), that these compounds possess the constitution previously assigned to them, and do not contain reduced anthraquinone nuclei. The anthragallol dimethyl ether (*A*), m. p. 209, when treated with alcoholic potassium acetate, gives the salt, $C_{16}H_{11}O_5K$, in violet-coloured leaflets, and on methylation forms *anthragallol trimethyl ether*, which crystallises in pale yellow needles, m. p. 167—168°. Anthragallol dimethyl ether (*B*) on methylation gives the same trimethyl ether, but the melting points of this dimethyl ether and its acetyl derivative, previously given as 225—227° and 175° respectively, are now found to be 230—232° and 176—178°. Experiments indicate that, whereas in the compound (*A*) the methoxy-groups are present in the positions 1 : 3, in (*B*) they occupy the positions 1 : 2. Alizarin α-methyl ether, m. p. 177—179°, on methylation gives alizarin dimethyl ether, m. p. 210—211°, and its acetyl compound, m. p. 212°, contains only one acetyl group. With potassium acetate, it gives a potassium salt, which forms garnet-red, prismatic needles.

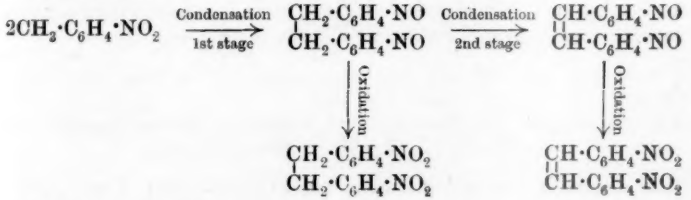
Hystazarin monomethyl ether on methylation gives *hystazarin dimethyl ether*, yellow needles, m. p. 235—236°, identical with the compound prepared from hystazarin itself. Finally, the natural *m*-hydroxyanthraquinone gave the methyl ether, m. p. 192—193°. The so-called anthragallol dimethyl ether (*C*) was previously isolated in so small an amount that it could not be profitably re-examined, but, as the description of Böck's dimethyl ether (*loc. cit.*) does not agree with that assigned to this compound, it is possibly not a distinct substance.

A re-examination of emodin monomethyl ether (Perkin and Hummel, *Trans.*, 1894, **65**, 923) has confirmed the properties, melting point, &c., previously assigned to it, so that Oesterle's conjecture that it is identical with his trihydroxymethylanthraquinone monomethyl ether (*Arch. Pharm.*, 1907, **245**, 287) is incorrect.

245. "The colouring matters of the stilbene group. Part IV. Action of caustic alkalis on para-nitrotoluene and its derivatives." By Arthur George Green, Arthur Hugh Davies, and Ronald Smith Horsfall.

The authors find that the product of oxidation of substituted *p*-nitrotoluenes under the influence of caustic alkalis is largely dependant on the reactivity of the particular compound employed, this being determined by the nature of the ortho-substituent. Thus, whilst the cyano-derivative (like the chloro-derivative and the phenyl sulphonate already investigated) gave only a stilbene derivative, dibenzyl compounds were obtained from the methyl, methoxy-, and carboxy-derivatives, and both stilbene and dibenzyl derivatives from *p*-nitrotoluene itself. Those derivatives which react least easily with production of red condensation products yield dibenzyl compounds by preference, whilst those which react most readily and form violet to blue condensation products give chiefly stilbene compounds.

The results point to the conclusion that the condensation in question occurs in two stages, which may be more or less concurrent according to the degree of reactivity of the substance. The product of the first stage, when oxidised, gives a dinitrodibenzyl, that of the second stage a dinitrostilbene:



Substituents which increase the reactivity of the substance therefore favour the formation of stilbene compounds.

A comparison of the relative reactivity of a number of such compounds under like conditions shows that, whilst the methyl, methoxy-, amino-, and carboxy-groups have but little influence on the reactivity, the more strongly electronegative groups, such as the sulphophenyl, cyano- and nitro-groups, exert a powerful effect, that of the nitro-group being the strongest.

246. "The replacement of alkyl radicles by methyl in substituted ammonium compounds." By Humphrey Owen Jones and John Robertshaw Hill.

It has been shown previously (*Proc.*, 1901, **17**, 265; *Trans.*, 1905, **87**, 1726) that the allyl and benzyl groups are readily displaced from amines or quaternary ammonium compounds by the methyl group on treatment with methyl iodide either at the ordinary temperature or at 100°.

The authors now find that the other alkyl groups, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl, are all replaced by methyl, sometimes in the cold, but more easily on heating with methyl iodide.

The two series of ammonium compounds derived from dimethylaniline and *p*-bromodimethylaniline (Hill, *Proc. Camb. Phil. Soc.*, 1907, **14**, 166) have been examined, and the phenyltrimethyl compound is the final product in each case. The replacement is due to the dissociation of the ammonium salt, in methyl iodide solution, into tertiary amine and alkyl iodide, the tertiary amine then combines with methyl iodide to produce the trimethyl compound, which is, in each case, much the least soluble of all. The ease with which the different groups are replaced varies considerably, and is dependent jointly on the extent to which the dissociation takes place and on the solubility of the ammonium salt. The ethyl or *iso*butyl group is most readily replaced, and the *iso*amyl group is the most difficult to displace.

247. "Note on the formation of abnormal platinichlorides. (A correction.)" By Albert Ernest Dunstan.

In a recent communication (Dunstan and Cleaverley, *Trans.*, 1907, **91**, 1619), the preparation of three platinichlorides of the general formula B_4,H_2PtCl_6 was described. These were thought to belong to a new type of platinichlorides, but this is now found to be a mistake, as Werner (*Ber.*, 1903, **36**, 147) had collected all instances of such abnormalities known up to that date. Subsequently, Morgan and Micklethwait (*Trans.*, 1906, **89**, 863) added the cases of coumarin platinichloride and aurichloride, whilst Pickard and Kenyon have described (*Trans.*, 1906, **89**, 268) triethyl-, tripropyl-, and tribenzylphosphine oxide hydrogen platinichlorides, the latter of which had been prepared by Fleissner (*Ber.*, 1880, **13**, 1665) and by Letts and Collie (*Trans. Roy. Soc. Edin.*, 1888, **30**, I, 181).

248. "The nitrates of dimethyl- and methylethyl-thetine menthyl esters." By Samuel Smiles.

The nitrates of dimethyl- and methylethyl-thetine menthyl esters were prepared by precipitating concentrated aqueous solutions of the bromides with aqueous ammonium nitrate. *Dimethylthetine* l-*menthyl ester nitrate* forms colourless prisms which melt at 125—127° and are very sparingly soluble in cold water or ethyl acetate, but readily so in the hot media. In alcoholic solution, (1) 2 per cent. the salt has $[\alpha]_D$ −53·9° and $[M]_D$ −173° approximately. *Methylethyl*-d-l-*thetine* l-*menthyl ester nitrate* has $[M]_D$ about −178° in the same solvent; it melts at 120—122°, and is slightly more soluble than the dimethyl derivative.

The methylethyl salt was fractionally crystallised from ethyl acetate with a view to resolving the thetine into optical isomerides. The experiments have been hitherto unsuccessful, probably owing to the instability of the ester to which attention has already been drawn (*Trans.*, 1905, **87**, 451). The less soluble fraction contained the dimethylthetine ester, indicating the decomposition of the salt. The rotatory powers of the platinichlorides of the dimethyl and methylethyl derivatives are corrected from these already given to $[M]_D$ −438° for the dimethyl and $[M]_D$ −380° approximately for the methylethylthetine, that for the diethyl being, as before, $[M]_D$ −330°.

249. Synthesis of brazilinic acid and the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids. (Preliminary note.) By William Henry Perkin, jun., and Robert Robinson.

Brazilinic acid is formed when trimethylbrazilin is oxidised by permanganate (*Trans.*, 1902, **81**, 1030):

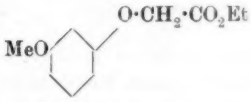
$$C_{19}H_{20}O_5 + O_5 = C_{19}H_{18}O_9 + H_2O,$$

and, on reduction, is converted into the lactone of dihydrobrazilinic acid:

$$C_{19}H_{18}O_9 + 2H = C_{19}H_{18}O_8 + H_2O.$$

Since these two acids contain the same number of carbon atoms as trimethylbrazilin, it seemed probable that the determination of their constitutions might yield information which would definitely prove the constitution of brazilin. The authors have succeeded in synthesising brazilinic acid, the lactone of dihydrobrazilinic acid, and also the corresponding lactone of dihydrohæmatoxylinic acid by methods which leave no doubt as to their constitutions.

Brazilinic acid (m. p. 208°) is obtained in small quantity when a mixture of *m*-methoxyphenoxyacetic ester and *m*-hemipinic anhydride



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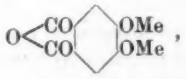
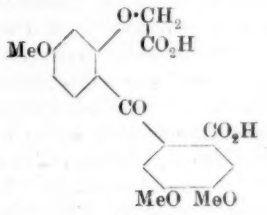
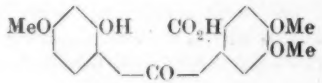


is dissolved in carbon disulphide and treated with aluminium chloride. This synthesis clearly indicated that brazilinic acid must be represented by the formula (I).



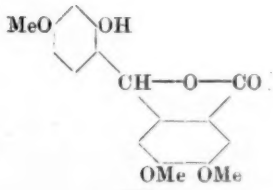
(I.)



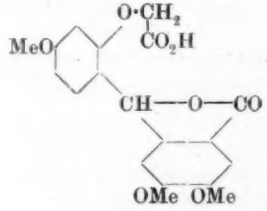
(II.)

and further proof of this was obtained by the synthesis of the *lactone* of *dihydrobrazilinic acid*, which was accomplished in the following way. A mixture of resorcinol dimethylether and *m*-hemipinic anhydride, when treated with aluminium chloride, yields *hydroxytrimethoxybenzoylbenzoic acid* (II).

Reduction with sodium amalgam converts this acid into *hydroxymethoxyphenyl*-m-*meconine* (m. p. 207°) (III):



(III.)

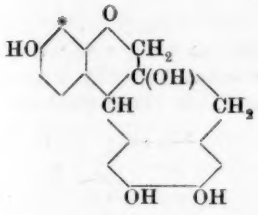


(IV.)

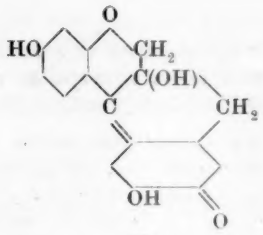
When this substance is treated with chloroacetic acid and potassium hydroxide, it is converted into an acid which melts at 226—227° and is identical with the *lactone* of *dihydrobrazilinic acid*.

The latter acid must therefore have the constitution (IV).

This synthesis not only confirms the constitution given above to brazilinic acid, but the authors consider that it proves clearly that brazilin must be represented by the constitutional formula (V),



(V.)

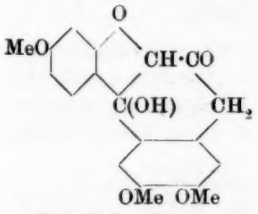


(VI.)

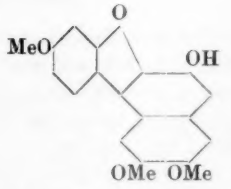
first suggested by Werner and Pfeiffer (*Chem. Zeitsch.*, 1904, **3**, 421).

The *lactone* of *dihydrohæmatoxylinic acid* (m. p. 192°) was similarly synthesised from pyrogallol trimethyl ether and *m*-hemipinic anhydride by treatment with aluminium chloride and subsequent reduction and treatment with potassium hydroxide and chloroacetic acid. The constitution for hæmatoxylin is therefore derived from the above formula for brazilin by the introduction of a hydroxy-group at the point indicated by the asterisk.

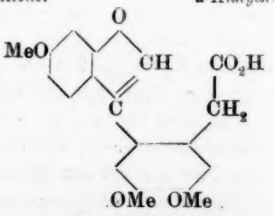
An entirely different series of experiments on brazilein, carried out in conjunction with Paul Engels, has shown that the constitution of this important substance is represented by (VI), an expression easily derived from the formula of brazilin given above. In the detailed account of the authors' experiments, it will be further shown that the important derivatives of trimethylbrazilin, namely, trimethylbrazilone, α-anhydrotrimethylbrazilone and ψ-trimethylbrazilone, have constitutions represented by the formulæ :



Trimethylbrazilone.



α-Anhydrotrimethylbrazilone.



ψ-Trimethylbrazilone.

250. "Condensations of ketones containing the group $\cdot CH_2 \cdot CO \cdot CH:$ with esters in presence of sodium ethoxide." By Reginald William Lane Clarke, Arthur Lapworth, and Elkan Wechsler.

It has already been shown (*Trans.*, 1907, **91**, 1919) that when cyanodihydrocarvone, which contains the above grouping, is acted on by nitrous esters in presence of sodium ethoxide, the attack occurs at the $\cdot CH:$ group. It is now proved that menthone reacts in the same way, although when alkyl formates are used under analogous conditions it is the $\cdot CH_2 \cdot$ group which is reactive. Pulegone appears first to be converted into *iso*pulegone, which then behaves like menthone, yielding a *hydroximino-acid* having the structure:

$$\begin{matrix} CH_3 \\ CH_2 \end{matrix} \!\!> C \cdot C(:NOH) \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CO_2H.$$

Bromocamphor yields only *iso*nitrosocamphor, and fenchone, in accordance with Semmler's view of its constitution, is quite unaffected.

The fact, that esters of different kinds, acting under the influence of sodium ethoxide and similar agents, appear to select different points for attack on ketones containing the group $\cdot CH_2 \cdot CO \cdot CH:$, is shown to be of considerable importance in connexion with the question of the mechanism of syntheses brought about by such agents.

251. "Acylogens and thiocarbamides." By Augustus Edward Dixon and John Taylor.

Following up their previous inquiries in the above direction (*Trans.*, 1907, **91**, 912. Compare also Dixon and Hawthorne, *ibid.*, 122), the authors have now studied the behaviour of certain acyl chlorides with allyl-substituted thiocarbamides, and of phenylthiocarbamide with halogenised acyl halides.

Acetyl chloride unites with allylthiocarbamide to form

$$C_3H_5 \cdot NH \cdot C(NH) \cdot SAc,HCl,$$

white crystals, melting at 103—104°. On withdrawal of the combined halogen acid by weak alkali, the acetyl group migrates with production of $C_3H_5 \cdot NAc \cdot CS \cdot NH_2$, m. p. 96°, the latter, when melted, undergoing further change into $C_3H_5 \cdot NH \cdot CS \cdot NHAc$, m. p. 74°; of these three isomeric forms, the first alone is basic.

With *ab*-phenylallylthiocarbamide, acetyl chloride yields *N*-phenylpropylene-ψ-thiourea (Prager, *Ber.*, 1889, **22**, 2992).

Methyl chlorocarbonate gives with *ab*-phenylallylthiocarbamide the compound $C_3H_5 \cdot NH \cdot C(NPh) \cdot S \cdot CO_2Me,HCl$, m. p. 87°; from this,

water eliminates the halogen acid, and the carboxymethyl group thereupon migrates to form $C_3H_5{\cdot}N(CO_2Me){\cdot}CS{\cdot}NHPh$, m. p. 83°. Ethyl chlorocarbonate behaves similarly, the hydrochloride melting at 96°, and yielding by treatment with water the corresponding trisubstituted thiocarbamide as a non-basic oil.

Chloroacetyl chloride and bromopropionyl bromide react readily with phenylthiocarbamide, but not to produce additive compounds; instead, two molecules of halogen acid are eliminated, one of which passes off, the other remaining combined with the product, a ring compound, either "phenylthiohydantoin," $PhN{:}C\begin{smallmatrix}NH{\cdot}CO\\ S\text{---}CH_2\end{smallmatrix}$, or its methylic homologue, as the case may be.

Acetyl chloride combines with benzyl-ψ-thiourea,

$$NH_2{\cdot}C(NH){\cdot}S{\cdot}CH_2Ph,$$

furnishing the hydrochloride of an acetyl derivative, and, conversely, benzyl chloride unites additively with acetylthiocarbamide; whether the products are identical or isomeric could not be decided, owing to the readiness with which they decompose yielding benzyl mercaptan.

252. "The alkyl compounds of gold." By William Jackson Pope and Charles Stanley Gibson.

The authors have prepared *monoethylauric dibromide*, $(C_2H_5)AuBr_2$, and *amminodiethylauric bromide*, $(C_2H_5)_2AuBr,NH_3$ (compare also *Proc.*, 1907, **23**, 245).

253. "The refractive power of diphenylhexatriene and allied hydrocarbons." By Ida Smedley.

The molecular refractions of diphenylbutadiene and diphenylhexatriene (*Proc.*, 1907, **23**, 162) were measured and compared with those of other hydrocarbons. Sufficient data have been obtained to calculate the influence of the phenyl and the ethenoid groups in unsaturated hydrocarbons. In each case, the refractive power of the group increases markedly as the number of unsaturated groups with which it is conjugated increases. The influence of the hexatriene structure is always greater than that of the benzene ring, a result considered by the author to be at variance with the representation of the benzene molecule as a closely conjugated system of double bonds.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Cohen, *Julius B.* Organic chemistry for advanced students. pp. viii + 632. London 1907. (*Recd.* 28/11/07.) From the Author.

Goppelsroeder, *Friedrich.* Neue Capillar- und Capillaranalytische Untersuchungen. pp. xiv + 81. ill. Basel 1907. (*Recd.* 22/11/07.) From the Author.

Hutton, *Frederick Wollaston.* The lesson of evolution. 2nd edition. pp. xxiv + 301. Printed for private circulation, [Erith] 1907. (*Recd.* 7/11/07.) From Mrs. F. W. Hutton.

Kingzett, *Charles Thomas.* Nature's hygiene and sanitary chemistry: containing also a special account of the chemical and hygienic characters of eucalyptus, pine and camphor forests, and some industries connected therewith. 5th edition. pp. xvi + 527. London 1907. (*Recd.* 27/11/07.) From the Author.

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Meyer, *Victor,* and **Jacobson,** *Paul.* Lehrbuch der organischen Chemie. 2 Auflage, Band I. i. 2. pp. 449—1060. Leipzig 1907. (*Recd.* 14/11/07.)

Wiley, *Harvey W.* Foods and their adulteration. Origin, manufacture, and composition of food products; description of common adulterations, food standards, and national food laws and regulations. pp. xii + 625. ill. London [printed in America] 1907. (*Recd.* 22/11/07.)

III. *Pamphlets.*

Borns, *Henry.* Die Elektrochemie in Jahre 1906. (From the *Chem. Industrie*, **30**, 1907.)

Burgess, *G. K.* Melting points of the iron group elements by a new radiation method. (From the *Bull. Bureau of Standards*, **3**, 1907.)

Neogi, *Panchanan.* Notes from the Chemical Laboratory of the Presidency College. Note No. 1. A new method of preparing mercurous iodide. (From the *J. and Proc. Asiatic Soc. of Bengal*, **3**, 1907.)

Sandberg, *Christer Peter.* The chemical composition of steel rails and latest improvements. (From the *Trans. Engineering Conference, Inst.C.E.*, 1907.)

Schaefer, *Theodore W.* The contamination of the air of our cities with sulphur dioxide, the cause of respiratory disease. (From the *Boston Med. and Surg. Jour.*, **157**, 1907.)

Svedberg, *The.* Studien zur Lehre von den kolloiden Lösungen. (From the *Nova Acta Reg. Soc. Sci. Ups.*, [iv], **2**, 1907.)

Watts, *Oliver Patterson.* An investigation of the borides and the silicides. (From the *Bull. Univ. Wisconsin. Engineering Ser.*, **3**, 1906.)

At the next Ordinary Meeting, on **Thursday**, December 19th, 1907, at **8.30** p.m., the following papers will be communicated:

"Derivatives of tetramethyl glucose." By J. C. Irvine and A. M. Moodie.

"The characterisation of mercerised cotton." (Preliminary note.) By J. Hübner.

"Attempted synthesis of $\begin{matrix}\beta\text{-N-}\beta\\ \beta\text{-CH-}\beta\end{matrix}$ dinaphthacridine: Condensation of methylene dichloride and *l*-substituted-2-naphthylamines." By A. Senier and P. C. Austin.

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Issued 30/12/07

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Vol. 23. **No. 334.**

Thursday, December 19th, 1907, at 8.30 p.m., Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

The President referred to the death of Lord Kelvin, and stated that the Society would be represented at his funeral.

It was also announced that the Society had lost through death Mr. Samuel Hall, and Prof. B. J. Harrington, of McGill University, Montreal.

Messrs. P. V. Dupré, G. H. Martin, C. P. Matthews, W. S. Mills, M. Wechsler, E. Wheeler, and R. Whymper were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs.:

Guy Barr, B.A., B.Sc., 79, Fillebrook Road, Leytonstone, N.E.

Walter Brown, jun., Brookvale, Strathaven, N.B.

David Cowan Crichton, M.A., B.Sc., A.I.C., Backhill House, Musselburgh.

Andrew L. Scott, F.I.C., Fir Lodge, Cheshunt, Herts.

John Armstrong Smythe, 15, The Poplars, Gosforth, Newcastle-on-Tyne.

Charles Sedgley Spiers, The Woodlands, Scalford Road, Melton Mowbray.

John Watson, B.Sc., 5, Kendrew Street, Darlington.
William Henry Withey, B.A., Stroud, Glos.
Joseph Yates, 18, Park Street, Haslingden, Lancs.

Certificates have been authorised by the Council under Bye Law I (3) in favour of the following:

Puran Singh, Dehra Dun, India.
Archibald Edgar Collens, Government Laboratory, Port of Spain, Trinidad.

Of the following papers, those marked * were read:—

***254. "Attempted synthesis of $\begin{matrix}\beta\text{–N–}\beta\\ \beta\text{–CH}\beta\end{matrix}$-dinaphthacridine; condensation of methylene dichloride and 1-substituted-2-naphthylamines." By Alfred Senier and Percy Corlett Austin.**

In attempting to synthesise derivatives of the unknown $\begin{matrix}\beta\text{–N–}\beta\\ \beta\text{–CH}\beta\end{matrix}$-dinaphthacridine (compare Senier and Austin, *Trans.*, 1906, **89**, 1387) by condensing methylene dichloride with derivatives of β-naphthylamine in which the hydrogen of the α-position adjacent to the amino-group had been substituted, the authors have found that when the substituent was a halogen, either Reed's dinaphthacridine or a meso-derivative thereof was formed, thus completing the proof that this base has the constitution assigned to it. In the case of 1-nitro-2-naphthylamine, no acridine was obtained.

1-Chloro-2-naphthylamine reacts with methylene dichloride to form $\begin{matrix}\beta\text{–N–}\beta\\ \alpha\text{–CH}\alpha\end{matrix}$-dinaphthacridine. 1-Bromo-2-naphthylamine and methylene dichloride yield 7-*bromo*-$\begin{matrix}\beta\text{–N–}\beta\\ \alpha\text{–CH}\alpha\end{matrix}$-*dinaphthacridine*, which crystallises from benzene in yellow needles, melting at 215·5° (corr.). Its solutions are fluorescent, and it differs from the halides of the dinaphthacridines (Senier and Austin, *Trans.*, 1904, **85**, 1196), as it may be boiled with potassium hydroxide solution, and even distilled under reduced pressure, without decomposition.

The *hydrochloride*, *aurichloride*, and *platinichloride* are yellow powders.

With glacial acetic acid, the base forms a deep yellow, crystalline *compound*, melting at 273°. Reduction with stannous chloride leads to the production of bis-$\begin{matrix}\beta\text{–N–}\beta\\ \alpha\text{–CH}\alpha\end{matrix}$-dinaphthacridine dihydride.

*255. "Cobaltamine compounds." (Preliminary note.)

By Charles Edward Groves.

During the past few years, the author has investigated some of the cobaltamine compounds, and owing to the recent appearance of papers on the subject, he considers it advisable to publish a preliminary account of some of the results obtained.

Crimson Carbonate.—When freshly-precipitated cobalt carbonate, suspended in dilute ammonia, is agitated with air and then exposed to the air for three or four days, the solution becomes brownish-red and deposits bright crimson crystals. These can be purified by recrystallisation from water at about 45°, or, better, from a very dilute solution of ammonium bicarbonate. The carbonate is readily decomposed by acids with evolution of carbon dioxide, and formation of the corresponding salts. It is almost insoluble in cold water, but on heating gently (45°) the crystals dissolve; at a higher temperature, the solution becomes brown and turbid. The substance is practically insoluble in dilute ammonia in the cold, and very little dissolves even on heating It is almost insoluble in dilute alcohol even on boiling. The author purposes, provisionally, calling this compound *carycino-cobaltamine carbonate* (καρύκινος, blood-red).

Blue-black Compound.—This is formed when the crimson carbonate is treated with nitro-hydrochloric acid. On gradually adding the latter to the carbonate under water, it dissolves with effervescence, but on adding more of the acid a red, crystalline precipitate is produced, which if left in the liquid for a day or more is converted into the "bluish-black" crystals. This compound dissolves readily in concentrated ammonia, forming a rose-coloured liquid. When boiled with hydrochloric acid, it is, apparently, completely converted into the purpureo-chloride. In an aqueous solution of ammonium bicarbonate, it dissolves to a purple liquid.

Bronze-green Chloride and the corresponding *Nitrate.*—Of these two salts, the nitrate is the more readily prepared, and it can be easily converted into the chloride, which is bronze-green, the colour of the nitrate being greyish-green. The nitrate is most easily prepared by gradually adding a solution of cobalt nitrate in dilute nitric acid, in the proper proportion, to a mixture of dilute ammonia with a solution of ammonium persulphate contained in a large flask, and, after it is thoroughly oxidised by shaking it with air, acidifying the mixture with dilute nitric acid.

This nitrate is almost insoluble in water, but dilute ammonia dissolves it readily, forming a pink solution, and it is also soluble in ammonium bicarbonate solution. It is neither altered nor dissolved

by nitric acid, whether concentrated or dilute, and it is also insoluble in boiling acetic acid, but on adding concentrated hydrochloric acid to the mixture it dissolves at once.

The hydrochloride is easily obtained from the nitrate by heating the latter with dilute hydrochloric acid (1 : 2) at 70° for twenty to twenty-five minutes. It can easily be recrystallised from hot very dilute hydrochloric acid, when it separates in long, bronze-green needles. The purified hydrochloride dissolves in cold water, forming a deep blue liquid, but this soon decomposes, especially when warmed, depositing a brown powder, apparently cobaltous-cobaltic oxide.

Grass-green Compound.—If purpureo-cobaltic chloride (or nitrate) is heated for some hours with dilute ammonia, or, better, ammonium carbonate solution, it dissolves, and the dark red solution containing roseo-cobaltic salt, if kept for some time, deposits a crystalline mass consisting of minute, pink needles. After these have been separated, concentrated nitric acid is added to the mother liquor, the brick-red precipitate thus formed is removed by filtration, and a slow current of crude nitrosyl chloride passed into the purple-red filtrate. This after twenty-four hours deposits a mixture of red and green crystals. These can be separated by washing with water, which easily dissolves the red crystals, leaving the grass-green compound, which is comparatively insoluble in water.

This green salt is only sparingly soluble in water and in dilute ammonium bicarbonate solution, and is practically insoluble in alcohol and dilute acids. When boiled with dilute hydrochloric acid, it appears to be converted into the purpureo-chloride.

***256. "The direct interaction of aryl halides and magnesium." By James Frederick Spencer and Eleanor Marguerite Stokes.**

The authors find that cyclic halogen compounds react with magnesium powder without the use of ether when the two substances are heated together. The products, which are of the type R·MgX, are light grey solids, and are readily decomposed by water with considerable evolution of heat and production of the hydrocarbon:

$$R{\cdot}MgI + H_2O = R{\cdot}H{\cdot} + Mg(OH)I.$$

Iodo- and bromo-benzene yielded benzene and diphenyl; *p*-iodo- and *o*-bromo-toluene gave toluene; *m*-bromo- and *o*-chloro-aniline gave aniline; *p*-bromo-phenol yielded phenol, and α-bromonaphthalene and bromoacenaphthene gave the respective hydrocarbons. The yields in all these cases were extremely good. Chloro-substitution products do

not react generally in this way. In the case of aliphatic compounds, methyl iodide, methylene iodide, and *iso*propyl iodide were indifferent, but bromosuccinic acid gave succinic acid.

Discussion.

Dr. McKenzie pointed out the interest of the observations of the authors in connexion with Tschelinzeff's results with the "individual" magnesium compounds of the type R·MgX, obtained by the interaction of magnesium and halogen compounds in benzene solution with the use of dimethylaniline as catalyst.

In view of the results of Schroeter (*Ber.*, 1903, **36**, 3005) on the action of carbon dioxide on magnesium phenyl bromide, Dr. McKenzie asked if the formation either of triphenylcarbinol or benzophenone had been noted by the authors in the experiment on the formation of benzoic acid described by them.

Dr. Spencer replied that, owing to the large yields obtained, triphenylcarbinol and benzophenone had not been looked for, and their formation could only take place to a small extent, if at all.

257. "Derivatives of tetramethyl glucose." By James Colquhoun Irvine and Agnes Marion Moodie.

Tetramethyl glucoseoxime, which was obtained as a mixture of α- and β-forms melting at 61—68°, shows in methyl-alcoholic solution a specific rotation of +25·9° without mutarotation. The constitution of the compound, deduced from its behaviour on alkylation and the hydrolysis of the product, shows that it does not possess the normal oxime structure, but is produced by the reaction of the sugar in its γ-oxidic forms. Similar arguments point to the fact that tetramethyl glucoseanilide also possesses the γ-oxidic linking, and is not derived from an alkyloxy-aldehyde. The compound melted at 132—134°, and gave $[\alpha]_D^{20}$ + 229·5° in acetone solution.

Tetramethyl chloroglucose and *tetramethyl bromoglucose* were obtained as uncrystallisable syrups, which, in their reactions, closely resemble the corresponding tetra-acetyl compounds. As they were readily converted into a mixture of α- and β-tetramethyl methylglucosides when treated with methyl alcohol and silver oxide, the preparations doubtless consisted of mixtures of α- and β-forms.

Negative results were obtained in attempts to produce acetal derivatives of tetramethyl glucose, and the application of the Grignard reaction also led to no result.

With one doubtful exception, all the derivatives studied indicate that the alkylated sugar reacts invariably in the γ-oxidic form, but

this characteristic linking appears to be absent in tetramethyl glucose-hydrazone.

In the course of the work, it was found that the silver oxide method of alkylation can be readily applied to the methylation of different types of oximes, thus furnishing a convenient method of determining the hydroxyl content of such compounds.

258. "The characterisation of mercerised cotton." (Preliminary note.) By Julius Hübner.

The author has studied the action of a number of reagents on cotton, both before and after mercerisation, and finds that the following methods afford a certain means of distinguishing between mercerised and non-mercerised cotton, and also enable the degree of mercerisation to be approximately ascertained.

The cotton to be examined is steeped in a saturated solution of potassium iodide containing iodine; after a few seconds' immersion, the sample is withdrawn and washed five or six times in a 2 per cent. potassium iodide solution. After this treatment, mercerised cotton is found to have acquired a brownish-black colour, whilst unmercerised cotton remains white; on then treating the samples with water, the mercerised cotton turns bluish-black and the unmercerised sample remains quite white.

Another convenient method for distinguishing between mercerised and untreated cotton consists in steeping the samples in an aqueous solution, 100 c.c. of which contain 93·3 grams of zinc chloride and about 0·005 gram of iodine; in this liquid, non-mercerised cotton remains practically white, whilst the mercerised material becomes of a dark navy-blue colour.

259. "Note on the action of metallic calcium on alcohols." By Frederick Mollwo Perkin and Lionel Pratt.

It has been stated that metallic calcium has no action on alcohol, and may therefore be employed as a dehydrating agent for alcohols. The authors find, however, that, when metallic calcium is allowed to remain in contact with ethyl or methyl alcohol for from thirty to sixty minutes, reaction ensues and may become very vigorous. Once started the reaction continues to completion, according to the equation: $2CH_3{\cdot}OH + Ca = (CH_3{\cdot}O)_2Ca + H_2$.

If the mixture is heated to the boiling point of the alcohol, the reaction proceeds much more rapidly. With propyl, *iso*butyl, amyl, and

benzyl alcohols, the reaction takes place exceedingly slowly at the ordinary temperature, but completes itself in the course of a few hours at the boiling point of the alcohol. Analysis shows the white, amorphous powder obtained in all cases to be $(Alk{\cdot}O)_2Ca$.

260. "Note on the iodates and periodates of the alkalis and the ammonium radicle." By Thomas Vipond Barker.

The author gave a description of rubidium periodate, together with an account of some specific gravity and solubility determinations of the iodates of rubidium and cæsium, and the periodates of sodium, potassium, rubidium, cæsium, and ammonium.

261. "The colour of cupric salts in aqueous solution." By Nevil Vincent Sidgwick and Henry Thomas Tizard.

The authors have measured the depth of colour of aqueous solutions of cupric salts from the point where they become blue, and the influence on it of the anion and the concentration, using the Donnan tintometer. The main results are:

(1) All the salts examined (propionate, acetate, formate, monochloroacetate, chloride, bromide, sulphate, nitrate) showed the same tint at dilutions greater than about $N/4$, but the depth of colour varied with the anion and the dilution. This shows that they contain at least two substances of the same tint, but of different depths of colour.

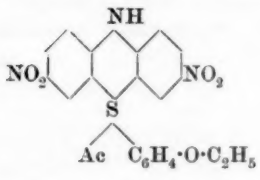
(2) The weak acid salts are deeply coloured at high concentrations, and the more so the weaker the acid. On dilution, the colour diminishes, tending to a value from two to four times that for copper sulphate, according to the acid, and hence greater than that of the cupric ion. It is therefore suggested that the change is due to the dissociation of CuA_2 into $CuA^{\cdot}$, which must then proceed very far before the second dissociation giving $Cu^{\cdot\cdot}$ ions begins. The second dissociation constant of a ternary salt, MX_2, should be very small, in accordance with Ostwald's theory for dibasic organic acids, as the positive charge on the metal in the ion $MX^{\cdot}$ will resist the appearance of a second charge on M.

(3) The salts of strong acids are always much paler than those of weak. On dilution the colour deepens, but only slightly. With copper nitrate, the complexes formed in very concentrated solution are of the same blue colour as the copper ion, but deeper.

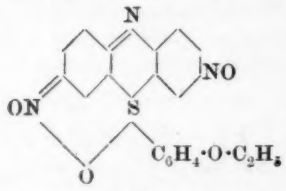
(4) It thus seems probable that ionisation affects the intensity of the colour, but not the tint.

262. "Derivatives of *S*-phenylphenazothionium." Part I. By Samuel Smiles and Thomas Percy Hilditch.

The α- and β-dinitro-compounds obtained from thiodiphenylamine by the action of nitric acid (Bernthsen, *Annalen*, 1885, **230**, 116) yield the sulphates of bases when condensed with phenetole in presence of concentrated sulphuric acid. Thus Bernthsen's view that these substances are sulphoxides is confirmed. The condensation products referred to are salts of *S*-phenetyl-3 : 3′-dinitrophenazothionium (I);



I.



II.

these are converted by aqueous alkali into the reddish-brown, fluorescent thetine (II). Hydrolysis of the salts furnishes the crimson sulphonium hydroxide. Derivatives of *S*-phenetyl-*N*-methylphenazothionium have been prepared in the same way; here, as with the above-mentioned compounds, the salts are green, but the base is dull brown and not fluorescent. A synthesis of these substances was attempted by the condensation of di-*p*-nitrodiphenylamine and phenetole-*p*-sulphinic acid, but the reaction could not be carried beyond the intermediate stage of the sulphoxide.

263. "A colorimetric method for the determination of small percentages of iron in copper alloys." By Arnold William Gregory.

The method is based upon the colour reaction given by salicylic acid and ferric chloride. This reaction is modified by using a solution of salicylic acid in acetic acid, and the test is carried out in the presence of sodium acetate. Under these conditions, a deep red colour is produced, which is used as a colorimetric test for iron in small quantities. The interfering action of the blue copper salts is overcome by the addition of a weak solution of potassium cyanide, which results in the formation of the colourless complex cyanide of copper and potassium.

Zinc and antimony do not interfere with the reaction, but lead must be removed as sulphate.

This method has been found to give very accurate results in cases where the percentage of iron in the copper alloys is so low that the ordinary gravimetric methods of estimation involve the use of a large quantity of the alloy.

264. "The effect of heat on the alkyl iodides." By Zelda Kahan.

Experiments on the effect of heating alkyl iodides alone and in the presence of zinc, sodium, silver chloride, and barium peroxide show that the probable course of the reaction is:

(1) The dissociation of the alkyl iodide into hydrogen iodide and an alkylene or alkylidene derivative.

(2) If alkylidene is formed, its conversion into an ethylene derivative.

(3) The reduction of the ethylene derivative by the hydrogen iodide. When heated alone, ethyl iodide yields ethane, ethylene, and a little hydrogen, but in the presence of zinc, butane is also formed in amount proportional to the quantity of zinc employed. Methyl iodide decomposes much less readily than any of the alkyl iodides, yielding chiefly methane and ethylene; with zinc, ethane is also formed, but with barium peroxide the chief products are carbon mono- and di-oxides and methane.

The normal and *iso*propyl iodides, when heated alone, yield only propane, but with zinc or sodium much propylene and some hydrogen are also formed.

265. "The influence of acids and alkalis on the velocity of formation of acetoxime." By Ernest Barrett and Arthur Lapworth.

At 0° and at a dilution of one gram-molecule each of acetone and hydroxylamine per 40 litres, the velocity of oxime formation is least with no other base or acid present. The acceleration caused by sodium hydroxide is very large and nearly proportional to the concentration of that substance. The acceleration caused by hydrochloric acid is also considerable, and rises rapidly until when half a gram-molecule of acid is present the velocity is more than fifty times as great as at first. With more acid, a very rapid fall occurs, and attains a nearly constant velocity when rather more than one gram-molecule of acid is present.

With acetaldehyde, very similar results were obtained.

The measurements were carried out before the appearance of Acree and Johnson's recent paper (*J. Amer. Chem. Soc.*, 1907, 38, 258).

266. "Action of metallic calcium on ketones." By Herbert Drake Law and Frederick Mollwo Perkin.

When metallic calcium is placed in contact with acetone which has previously been dried over calcium chloride, a slow evolution of hydrogen takes place, which becomes brisker in the course of a few hours. The rate of evolution of gas is about 2 litres in twenty-four hours at an average temperature of 16°. If the calcium and acetone are allowed to remain in contact for about one week and the product then fractionated, about 200 to 300 grams of mesityl oxide are obtained from 2 litres of acetone. More complex substances are also formed in considerable amount. If the acetone remaining after fractionation is again placed in contact with the same quantity of calcium, a further yield of mesityl oxide is obtained. The proportions for which the best results have been obtained are about 150 grams of metallic calcium and 2 litres of acetone. After standing for four days, 200 to 300 grams of mesityl oxide are obtained. When acetone is heated with metallic calcium, it is difficult to stop the reaction at the right point to obtain mesityl oxide, and products of high boiling point are formed.

Methyl ethyl ketone reacts very much more slowly with calcium, and the substances require to be left in contact for several months. When 1500 c.c. of methyl ethyl ketone are allowed to remain in contact with 200 grams of calcium for about one week, the rate of evolution of hydrogen is about 1 litre in twenty-four hours. On fractionation, at the end of eight to ten weeks, a considerable quantity of a fraction boiling at 164—165° is obtained, and also a larger quantity of fractions boiling up to 300°. The lower fraction is probably *γ-methyl-Δγ-heptene-ε-one*,

$$CH_3 \cdot CH_2 \cdot C(CH_3) : CH \cdot CO \cdot CH_2 \cdot CH_3.$$

On oxidation with potassium permanganate, acetic acid and methyl ethyl ketone are obtained. This does not actually prove the correctness of the formula just given, because the same results would be obtained by oxidation of the compound:

$$CH_3 \cdot CH_2 \cdot C(CH_3) : C(CH_3) \cdot CO \cdot CH_3.$$

The substance is a colourless liquid, having a very fragrant odour resembling that of oil of bergamot.

267. "The so-called 'tetrabromodiphenoquinone' and the constitution of coerulignone." By James Moir.

The author has continued his researches on Magatti's tetrabromodiphenoquinone (*Proc.*, 1906, **22**, 110), and has studied the action of reducing agents on this compound.

268. "A note on certain pyrogenic reactions." By Norman Thomas Mortimer Wilsmore and Alfred Walter Stewart.

In the course of some investigations on the effect of a white-hot platinum wire on various organic substances, the authors have made the following observations. The apparatus employed was in essentials the same as the generator used in the case of keten (*Trans.*, 1907, **91**, 1938). The results obtained were qualitative only, no analysis being made.

Owing to its possible use as a solvent, the behaviour of benzene was investigated; it was not affected by the wire, and toluene also was unacted on.

When ethyl crotonate is treated pyrogenically, ethylene is liberated, and crotonic acid crystallises from the cooled liquid which remains in the generator. An unsaturated acid, namely, cinnamic, was then tried in benzene solution, but no effect was observed. On the other hand, when saturated ethereal salts were placed in the generator, a mixture of carbon dioxide and hydrocarbons was liberated. The decomposition, in the case of ethyl acetate, appears to take place in the following steps

$$CH_3{\cdot}CO_2{\cdot}C_2H_5 \longrightarrow CH_3{\cdot}CO_2H + C_2H_4 \longrightarrow CH_4 + CO_2 + C_2H_4.$$

In the case of ethyl malonate, ethylene is first evolved, as in the foregoing case, and the malonic acid thus formed breaks down into carbon dioxide and acetic acid, whi h, in its turn, decomposes into methane and carbon dioxide. It is to be noted that whenever any acetyl derivative is formed in the course of any of these stages, some keten is in turn produced from it. In contradistinction to the behaviour of the fatty acids, benzoic acid in benzene solution was not noticeably attacked.

From these results, the authors conclude that the ethylenic linking in the α-position with respect to the carboxyl group tends to render the compound more stable with regard to this agent than is an ethane derivative. This view is, of course, supported by the fact that unsaturated hydrocarbons are more stable in the electric arc than saturated ones.

From acetone, keten was obtained, whilst substances of high boiling point, such as anethole and aniline, were decomposed with charring.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Bolduan, *Charles Frederick.* Immune sera. A concise exposition of our present knowledge concerning the constitution and mode of action of antitoxins, agglutinins, hæmolysins, bacteriolysins, precipitins, cytotoxins, and opsonins. 2nd edition, rewritten. pp. viii + 154. New York 1907. (*Recd.* 10/12/07.)
From the Publishers: Messrs. John Wiley and Sons.

Cross, *Charles Frederick,* and **Bevan,** *Edward John.* A text-book of paper-making. 3rd edition, containing additional matter, and in part re-written, with collaboration of *J. F.* **Briggs.** pp. x + 411. ill. London 1907. (*Recd.* 20/12/07.) From the Author.

Pawlewski, *Bronislaw.* Organiczna preparatyka chemiczna. pp. iv + 298 + iv. ill. Lwów 1908. (*Recd.* 19/12/07.) From the Author.

Rideal, *Samuel.* Sewage and the bacterial purification of sewage. 3rd edition. pp. xii + 355. ill. London 1906. (*Recd.* 18/12/07.) From the Author.

Weston, *Frank Edwin.* A scheme for the detection of the more common classes of carbon compounds. 2nd edition. pp. viii + 95. ill. London 1907. (*Recd.* 16/12/07.) From the Author.

At the next Ordinary Meeting on **Thursday,** January **16th,** 1908, at **8.30 p.m.,** the following papers will be communicated:

"Colour and constitution of azo-compounds. Part II. The salts of *p*-hydroxyazo-compounds with mineral acids." By J. J. Fox and J. T. Hewitt.

"The oxidation of aromatic hydrazines by metallic oxides, permanganate, and chromates." By F. D. Chattaway.

"Studies in fermentation. II. The mechanism of alcoholic fermentation." By A. Slator.

"Organic derivatives of silicon. Part IV. The sulphonation of benzylethylpropylsilicyl oxide and of benzylethyldipropylsilicane." By H. Marsden and F. S. Kipping.

"The formation and reactions of imino-compounds. Part VI. The formation of derivatives of hydrindene from dicyano-*o*-xylene." By C. W. Moore and J. F. Thorpe.

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